The Phos4You partnership

September 2021

Technical report
of the Phos4You partnership
on processes to recover phosphorus from wastewater

EGLV
Lippeverband
Interreg North-West Europe
Phos4You
European Regional Development Fund

Technical report of the Phos4You partnership on processes to recover phosphorus from wastewater

MOBILISE	*DEMONSTRATE*	*IMPLEMENT*
Phosphorus	**Recovery**	**Processes**
from wastewater	in real environment	for large & small WWTPs

edited by

LIPPEVERBAND
Ploteau, Marie-Edith; Althoff, Anke; Nafo, Issa; Teichgräber, Burkhard

Impressum

This report was prepared by the partners of the Phos4You project, funded through INTERREG VB North-West Europe programme (2014-2020) under the grant NWE292.

DOI number: https://doi.org/10.17185/duepublico/74788

Please cite this report and its contributions as follows:

Ploteau Marie-Edith, Althoff Anke, Nafo Issa, Teichgräber Burkhard, “Technical report of the Phos4You partnership on processes to recover phosphorus from wastewater”, September 2021, edited by LIPPEVERBAND, DOI n° 10.17185/duepublico/74788

and

Individual chapters are to be cited by naming the authors listed in each case.

Editor: LIPPEVERBAND
Kronprinzenstrasse 24
45128 Essen
Tel: +49 201 1040
www.eglv.de

First edition

September 2021

Essen (Germany)

Technical report of the Phos4You partnership on processes to recover phosphorus from wastewater

List of contributors

Ploteau, Marie-Edith [1]
Althoff Anke [1]
Blöhse, Dennis [1]
Nafo, Issa[1]
Léonard, Angélique [2]
Pfennig, Andreas [2]
Shariff, Zaheer [2]
Leleu, David [2]
Groslambert, Sylvie [2]
Chantrain, Gaspard [2]
Daumer, Marie-Line [3]
Bareha, Younes [3]
Harrington, Joe [4]
Barnett, Denise [4]
Power, Niahm [4]
Siddiqui, Asif [4]
O´Donnell, Ciaran[4]
Nättorp, Anders [5]
Escudero, Ania [6]
Reichelt, Lena-Dorothea [6]
Pahl, Ole [6]
Bremner, Barbara [7]
Papp, Szabolcs [7]
Taggart, Mark [7]
Vedrenne, Fabien [8]
Cunha, Marisa [8]
Mébarki, Cédric [8]
Schmelz, Karl-Georg [9]
Klein, Daniel [9]
Pamuk, Levent [9]
Teichgräber, Burkhard [9]
Zepke, Frank [10]

[1] Lippeverband, [2] Université de Liège, [3] Institut national de recherche pour l'agriculture, l'alimentation et l'environnement, [4] Munster Technological University, [5] Fachhochschule Nordwest Schweiz, [6] Glasgow Caledonian University, [7] Environmental Research Institute, The North Highland College, University of the Highlands and Islands, [8] Veolia Environnement, [9] Emschergenossenschaft, [10]EuPhoRe GmbH

September 2021

Picture credit on first page: Till Möller † /LIPPEVERBAND

Abstract in four languages (EN, DE, FR, NL)

[EN] To address the growing European requirements in regard with phosphorus (P), essential nutrient but finite resource, a main purpose of the Phos4You project was to make the proof of technologies to recover P from wastewater. For this, new or existing demonstrators were used to upscale innovative processes and/or validate emerging technologies in live, operational-scale environments. This was applied to recover P from large wastewater treatment plants (WWTP) or related sewage sludge incineration plant, as well as from small WWTPs. In all cases, the recovery of valuable phosphorus materials and by-products was aimed at. The Life Cycle Assessment (LCA) was carried out for some of the most advanced processes. Three different wet-chemical processes (TetraPhos®, Phos4Life™, PARFORCE) for leaching the P contained in sewage sludge ash (SSA), with the aim of producing a marketable phosphoric acid and reusable by-products from SSA with low P content, were successfully tested. A thermochemical process (EuPhoRe®) producing SSA directly usable in fertilising products was validated. Two processes starting with a biological or a chemical leaching (Struvia™ with bio-acidification step, PULSE) successfully produced phosphate salts. Three processes removing P at small-scale WWTPs were successfully demonstrated (microalgae photobioreactor, Filtraflo™-P using adsorbent prepared out of crab-carapace, Struvia™ applied for WWTP-effluent). The LCA of the processes adopted the “system extension” and the “avoided burden” approaches, both leading to similar conclusions. Environmental advantage in terms of the mineral resource depletion were confirmed for all P-recovery processes studied whereas the beneficial effects on other categories such as climate change and fossil fuel depletion were variable between the different systems. All results of the demonstrations were the base to prepare the deployment of P-recycling in urban and rural regions.

[DE] Um den wachsenden europäischen Anforderungen in Bezug auf Phosphor (P) - essentieller Nährstoff, aber endliche Ressource - gerecht zu werden, war das Hauptziel des Phos4You-Projekts, den Nachweis zur technischen Rückgewinnung von P aus Abwasser zu erbringen. Zu diesem Zweck wurden neue oder bestehende Demonstratoren betrieben, um innovative Prozesse hochzuskalieren und/oder sich entwickelnde Technologien im Betriebsmaßstab unter realen Bedingungen zu validieren. Dies wurde sowohl für die Rückgewinnung von P aus großen Kläranlagen (KA) oder zugehörigen Klärschlammverbrennungsanlagen als auch aus kleinen KA angewandt. In allen Fällen wurde die Rückgewinnung von verwertbaren phosphorhaltigen Materialien und Nebenprodukten angestrebt. Die Ökobilanzierung (LCA) wurde für einige der am weitesten fortgeschrittenen Verfahren durchgeführt. Drei

verschiedene nasschemische Verfahren (TetraPhos®, Phos4Life™, PARFORCE) zur Auslaugung des in Klärschlammasche (KSA) enthaltenen P wurden erfolgreich getestet mit dem Ziel, eine marktfähige Phosphorsäure und wiederverwertbare Nebenprodukte aus KSA mit geringem P-Gehalt herzustellen. Ein thermochemisches Verfahren (EuPhoRe®) zur Herstellung von KSA, die direkt in Düngemitteln verwendet werden können, wurde validiert. Zwei Prozesse, die mit einer biologischen oder chemischen Auslaugung beginnen (Struvia™ mit Bio-Versäuerung, PULSE), produzierten erfolgreich Phosphatsalze. Drei Prozesse zur Entfernung von P in kleinen Kläranlagen wurden erfolgreich demonstriert (Mikroalgenphotobioreaktor, Filtraflo™-P mit Adsorptionsmittel aus Krabbenpanzern, Struvia™ für Kläranlagenabwässer). Bei der Ökobilanz der Verfahren wurden die Ansätze "Systemerweiterung" und "vermiedene Belastung" angewandt, die beide zu ähnlichen Schlussfolgerungen führten. Für alle untersuchten P-Rückgewinnungsverfahren wurden Umweltvorteile in Bezug auf die Erschöpfung mineralischer Ressourcen bestätigt, während die positiven Auswirkungen auf andere Kategorien wie den Klimawandel und die Erschöpfung fossiler Brennstoffe bei den verschiedenen Systemen unterschiedlich ausfielen. Alle Ergebnisse der Demonstrationen waren die Grundlage für die Vorbereitung des Einsatzes von P-Recycling in städtischen und ländlichen Regionen.

[FR] Pour répondre aux enjeux croissants de l'Europe en matière de phosphore (P), nutriment essentiel mais ressource limitée, un des principaux objectifs du projet Phos4You était de faire la preuve des technologies de récupération du P dans les eaux usées. Pour ce faire, des démonstrateurs nouveaux ou pré-existants ont été utilisés pour améliorer des procédés innovants et/ou valider des technologies émergentes dans des environnements réels, à l'échelle opérationnelle. Cette démarche a été appliquée pour la récupération du phosphore depuis de grandes stations d'épuration des eaux usées (STEP) ou des installations d'incinération des boues d'épuration correspondantes, ainsi que depuis de petites STEP. Dans tous les cas, l'objectif était de récupérer des matières phosphatées et des co-produits valorisables. L'analyse du cycle de vie (ACV) a été réalisée pour certains des procédés les plus avancés. Trois différents procédés chimiques acides (TetraPhos®, Phos4Life™, PARFORCE) ont été testés avec succès pour la lixiviation du P contenu dans des cendres de boues d'épuration ayant une faible teneur en P, dans le but de produire un acide phosphorique commercialisable et des co-produits réutilisables. Un procédé thermochimique (EuPhoRe®) produisant des centres de boues directement utilisables dans les produits fertilisants a été validé. Deux procédés commençant par une lixiviation, biologique ou chimique (Struvia™ avec étape de bio-acidification, PULSE), ont produit avec succès des sels phosphatés. Trois procédés d'élimination du P dans des STEP de petite dimension ont été démontrés avec succès (photobioréacteur à microalgues, Filtraflo™-P utilisant un adsorbant préparé à partir de carapace de crabe, Struvia™ appliqué aux effluents de STEP). L'ACV des procédés a adopté les approches "extension du système" et "produits évités", qui ont toutes deux abouti à des conclusions similaires. Les avantages environnementaux en termes d'épuisement des ressources minérales ont été confirmés pour tous les procédés de récupération du P étudiés, tandis que les effets bénéfiques sur d'autres catégories telles que le changement climatique et l'épuisement des combustibles fossiles étaient variables entre les différents systèmes étudiés. Tous les résultats des démonstrations ont servi de base pour préparer le déploiement du recyclage du P dans les régions urbaines et rurales.

[NL] Om tegemoet te komen aan de groeiende Europese vraag naar fosfor (P), een essentiële voedingsstof maar eindige hulpbron, was een van de hoofddoelen van het Phos4You-project het testen van technologieën om P uit afvalwater terug te winnen. Daartoe werden nieuwe of bestaande demonstratiemodellen gebruikt om innovatieve processen op te schalen en/of opkomende technologieën te valideren in een omgeving op operationele schaal. Dit werd toegepast om P terug te winnen uit grote afvalwaterzuiveringsinstallaties (RWZI's) of daarmee verbonden zuiveringsslibverbrandingsinstallaties, alsook uit kleine RWZI's. In alle gevallen werd gestreefd naar de terugwinning van waardevolle fosforstoffen en bijproducten. De levenscyclusanalyse (LCA) werd uitgevoerd voor sommigen van de meeste geavanceerde processen. Drie verschillende nat-chemische processen (TetraPhos®, Phos4Life™, PARFORCE) voor het uitlogen van de P in zuiveringsslibas (SSA), met het oog op de productie van een verhandelbaar fosforzuur en herbruikbare bijproducten uit SSA met een laag P-gehalte, werden met succes getest. Een thermochemisch proces (EuPhoRe®) voor de productie van SSA dat rechtstreeks bruikbaar is in meststoffen, werd gevalideerd. Twee processen die starten met een biologische of een chemische uitloging (Struvia™ met bio-verzuringsstap, PULSE) produceerden met succes fosfaatzouten. Drie processen voor de verwijdering van P in kleinschalige RWZI's werden met succes gedemonstreerd (microalgenreactor, Filtraflo™-P met gebruikmaking van adsorptiemiddel bereid uit carapaces van kreeftachtigen, Struvia™ toegepast op RWZI-effluent). Voor de LCA van de processen werden de "systeemuitbreiding" en de "vermeden belasting" benadering gebruikt, die beide tot soortgelijke conclusies leidden. De milieuvoordelen met betrekking tot de uitputting van de minerale hulpbronnen werden bevestigd voor alle bestudeerde processen voor de terugwinning van P, terwijl de gunstige effecten op andere categorieën zoals klimaatverandering en de uitputting van fossiele brandstoffen varieerden tussen de verschillende systemen. Alle resultaten van de demonstraties vormden de basis voor de voorbereiding van de invoering van P-recycling in stedelijke en rurale omgevingen.

Executive summary

Background

The challenges caused by the nutrient phosphorus are tackled in various ways in the European Union, but always with the converging aim of avoiding potential damages caused by phosphorus excess in waterways while avoiding the losses of this finite resource, essential for all living organisms. The legal and regulatory framework in the EU and in some Member States, as well as further entrepreneurial initiatives are supporting the necessary technological developments to achieve a circularity in the management of phosphorus flowing through the wastewater.

Addressed issue

A number of phosphorus recovery technologies have been developed in the lab scale in the past decades. The variety of the technologies proposed answers the variety of situation where they can be applied. In Phos4You, the selection of the technologies aimed at reflecting the diversity of situations in which the recovery of phosphorus can occur.

Basically, in North-West Europe it can be distinguished between regions of urban nature and regions of rural nature. In a simplified view, the urban regions are equipped with large wastewater treatment plant that retains the phosphorus in a tertiary treatment. This phosphorus ends in sewage sludge and its nutrient value is lost when the sewage sludge gets incinerated, or if its availability for plants is compromised by the treatment of the sewage sludge or, even if plant available, when the sludge is not spread on soils. For this case, Phos4You scaled up technical solutions to recover the phosphorus from the sewage sludge ashes or from the sewage sludge out of large wastewater treatment plants.

In rural regions, there is up to now generally no recovery of phosphorus but increasingly this is recognised as a limiting factor for further developments especially in case of catchments sensitive for eutrophication. For this case, Phos4You looked at technical solutions to remove the phosphorus from the wastewater or from the wastewater effluent of small wastewater treatment plants. In the context of avoiding nutrient losses, the technical developments should ensure that the removed materials could be used as fertilising products.

By the scaling up of the technologies in real environment, the project aimed at making the proof of concept of processes and at giving solid information on which the further deployment of phosphorus recycling in different regions can be prepared.

Main findings

During the project lifetime (2016-2021), four P-recovery processes for large wastewater treatment schemes and three P-removal processes for small wastewater treatment schemes were demonstrated. The demonstrations occurred either with the setting up and operation of new pilot plants, or with pre-industrial testings carried out at existing pilot plants. Partners cooperated all alongside the implementation to support joint implementation and exchange on results and experiences.

Technically, all solutions were successful in achieving the production of phosphorus materials and by-products that can be recycled in the existing value chains. The achieved recovery rates were compliant with the legal requirements where such requirements do exist (e.g. in Germany).

For the recovery of phosphorus from sewage sludge ashes, the two technologies fully tested (TetraPhos® and PARFORCE) were successful in achieving the production of phosphoric acid from sewage sludge ashes having a low P- content (the Phos4Life™ process was also successfully tested, but only for the first steps). A recovery rate over 80 % was achieved. Both technologies also managed to cope with SSA with a high percentage of industrial sewage sludge, but for this, process adjustments and/or additional technical steps were required. The main technical differences between those processes - in terms of elution agent or process steps to remove impurities - led to the production of difference by-products and residues. The quality of those by-products (Gypsum, Fe-/Al-chloride, Fe-/Al-salt solution, brine or road salt, metal concentrate, $FeCl_3$) were roughly assessed to be recyclable in existing value chains.

For the recovery of phosphorus from sewage sludge, the three technologies implemented into demonstrators (EuPhoRe®, Struvia™ optimised with a bio-acidification reactor and PULSE) were successful in achieving the production of sewage sludge ashes or phosphate salts usable as components of fertilising products. To achieve the heavy metals reduction within the thermochemical treatment of sewage sludge, just a low amount of additives was necessary while the pyrolysis enabled the phosphorus to stay bioavailable for the crops despite of the post-combustion. The leaching of the phosphorus in the sewage sludge phase (either biologically for Struvia™ or chemically for PULSE) before the precipitation of phosphorus proofed in both cases to be a necessary step to achieve a recovery rate of the overall process of at least 50 % (as required e.g. by German legislation). The metal reduction was successfully achieved in both cases. For the chemical leaching, a dried sludge presented advantages in terms of handling and solid-liquid separation. For the biological leaching, the use of a low-cost co-substrate is essential to achieve an economic balance. The phosphates in the form of

HAP (hydroxyapatite) or other calcium phosphate salts usable in fertilising products after proper incorporation.

For the recovery of phosphorus at small-scale wastewater treatment plants, three technologies were demonstrated (microalgae photobioreactor; P-adsorption with Filtraflo™-P using CCM adsorbent; Struvia™). All were successful in reducing effluent P values to below 1.7 to 0.5 mg/L (compliant with EU discharge requirements for WWTPs discharging into sensitive areas potentially subject to eutrophication, currently only valid for WWTP>10,000 p.e). In all three processes, the recovered materials (microalgae biomass, P-rich biomass, calcium phosphate) showed fertilising properties. Using the *Chlamydomonas acidophila* microalgae, the process covered at once a secondary and a tertiary treatment and proved to be very robust, as well as working at very low light intensity. In the case of the Filtraflo™-P (using an activated adsorbent from crab-carapace) and Struvia™, effective tertiary treatment was shown. The conditions to create an optimised CCM (Chitosan-Calcite Material) adsorbent from seafood waste were also determined. With the downscaled Struvia™ process, the removal and recovery of phosphorus led to simultaneous reductions in total nitrogen and COD in effluent.

In addition to the technical study of the demonstrators, an environmental evaluation was conducted. By quantifying the impacts on the environment of the demonstrators and comparing them to the impacts of the reference system in which the recovery technologies were implemented, the study helped to highlight the most impactful steps from an environmental point of view and then to formulate eco-design advice. Two methodological approaches in the life cycle assessment were used: the system expansion and the avoided burden methodology. Sensitivity analyses were also performed on two parameters during the assessment, respectively the location of the recovery plant and the P_2O_5 content of the sewage sludge. For all P-recovery processes studied, an environmental advantage in terms of the mineral resource depletion category was assessed and confirmed to be significant. Beneficial effects on other LCA-categories such as global warming over the conventional chemical route to produce P fertiliser were showed for some of the P-recovery systems.

Recommendations

The further upscale of the demonstrated technologies can be recommended as the processes showed to be viable. Some upscales are already in preparation; some other were hampered through the Covid pandemic. Further use of the results are presented in the quality assessment report (Bogdan et al. 2021) and in the final report of Phos4You (Ploteau et al. 2021).

Acknowledgments

This work has been possible thanks to the support of many colleagues from the partners organizations involved in, associated to and external of the project Phos4You. The authors express their gratitude to the INTERREG VB North-West Europe Programme (2014-2020) for having trusted the partnership with the achievement of the project and co-funded the financial effort out of the European Regional Development Fund.

Acronyms and Abbreviations

ACP	Amorphous calcium phosphate
ADM	Anaerobic Digestion Model
AIDE	Association Intercommunale pour le Démergement et l'Epuration des communes de la province de Liège
AQ2	SEAL AQ2 Discrete Analyser (Seal Analytical, UK)
BBD	Box-Behnken design
BET	Brunauer–Emmett–Teller
BMP	Biomethanogen potential
BPD	Biological Phosphorus Dissolution
BPDP	Biological Phosphorus Dissolution Potential
C.	*Chlamydomonas*
CaP	Calcium phosphate
CCM	Chitosan-Calcite Material
CIT	Cork Institute of Technology *(merged into MTU*)
COD	Chemical Oxygen Demand
CPD	Chemical Phosphorus Dissolution
CRM	Certified Reference Materials
DS	Dry Substance
DM	Dry Matter
DOC	Dissolved Organic Carbon
DPP	Deutsche Phosphor Platform (German phosphorus platform)
EDX	X-ray pulse processor
EG	EMSCHERGENOSSENSCHAFT
EBPR	Enhanced biological phosphorus removal
EoL	End of Life
ERI	Environmental Research Institute, The North Highland College, University of the Highlands and Islands
ESPP	European Sustainable Phosphorus Platform
EU	European Union
FHNW	Fachhochschule Nordwestschweiz
FM	Fresh matter
FTIR	Fourier-transform infrared spectroscopy
FU	Functional Unit
GCU	Glasgow Caledonian University
GWP	Global Warming Potential
HAP	Hydroxyapatite

HRT	Hydraulic Retention Time
HVC	N.V. HVC Groep
ICP-OES	Inductively coupled plasma optical emission spectroscopy
INRAE	Institut national de recherche pour l'agriculture, l'alimentation et l'environnement.
IR	Impregnation Ratio
IUPAC	International Union of Pure and Applied Chemistry
L/D	light/dark
LCA	Life Cycle Assessment
LCC	Life Cycle Costing
LCV	Lower Calorific Value
LV	LIPPEVERBAND
Monetite	Dicalcium phosphate
MS	Mineral Solid
NPDES	National Pollution Discharge Elimination System
NWE	North-West Europe
OCP	Octacalcium phosphate
OD	Optical density
OWTS	Onsite wastewater treatment systems
O/A	Organic/aqueous
P	Phosphorus
P4Y	Phos4You
PAM	Polyacrylamide
PAO	Polyphosphate Accumulating Organisms
PE	Population Equivalent
PBR	Photobioreactor
PFO	Pseudo-First Order
PLC	Programmable Logic Controller
PPE	Personal Protective Equipment
PSO	Pseudo-Second Order
QA/QC	Quality Assurance/ Quality Control
RAS	Return Activated Sludge
rpm	Revolutions per minute
RSD	Response Surface Design
RRI	Remote, Rural and Island
S/L	Solid/liquid
SEM	Scanning Electron Microscope
SNB	N.V. Slibverwerking Noord-Brabant

SSA	Sewage sludge ashes
SSIP	Sewage Sludge Incineration Plant
STDV	Standard Deviation
SVA	Schlammverbrennungsanlage
SW	Scottish Water
TFF	Tangential Flow Filter
TKN	Total Kjeldahl Nitrogen
TON	Total Oxidable Nitrogen
TN	Total Nitrogen
TS	Total Solid
TSP	Triple Super Phosphate
TSS	Total Suspended Solids
UGent	Universität Gent
ULiège	Université de Liège
USGS	United States Geological Survey
VFA	Volatile fatty acid
VS	Volatile Solids
XRD	X-ray diffraction
XRPD	X-Ray Powder Diffraction
WFA	Wirbelschichtfeuerungsanlage
WFD	Water Framework Directive
WP	Work Package
MTU	Munster Technological University
WWTP	Wastewater treatment plant

Contents

List of contributors **4**

Abstract in four languages (EN, DE, FR, NL) **5**

Executive summary **9**

Acknowledgments **12**

Acronyms and Abbreviations **13**

1 Introduction **33**

1.1 Background of technical phosphorus recovery in North-West Europe 33

1.2 Objectives of a network of demonstrators 34

1.3 Scope of document 35

2 Overall set up of the network of demonstrators **36**

2.1 Overview of the work package dedicated to P-recovery technologies 36

2.2 Selection of the demonstrated technologies 37

2.3 Selected LCA-LCC approach 39

3 Demonstration of phosphorus recovery solutions **42**

3.1 Demonstrator I2: Acid extraction of P from SSA (REMONDIS TetraPhos®, PARFORCE, Phos4Life™) .. 42

3.1.1 Preparation of I2 .... *44*

3.1.2 Execution of I2 .... *49*

3.1.3 Analyses of results of I2 operations *51*

3.1.4 Discussion of results for I2 operation *77*

3.1.5 Conclusion for I2 .... *78*

3.2 Demonstrator I1: Thermochemical solution to recover P from sewage sludge (EuPhoRe®) 80

3.2.1 Preparation of I1 .... *81*

3.2.2 Execution of I1 .... *82*

3.2.3 Analyses of results of I1 operation *90*

3.2.4 Discussion of results for I1 operation *96*

3.2.5 Conclusion for I1 .... *97*

3.3 Demonstrator I6.1: Bio-acidification before P precipitation from sludge (optimised Struvia™) 98

3.3.1 Preparation of I6.1 .... *98*

3.3.2 Execution of I6.1 .... *110*

3.3.3 Analyses of results of I6.1 operation *113*

3.3.4 Discussion of results for I6.1 operation *118*

3.3.5 Conclusion for I6.1 .... *119*

3.4 Demonstrator I3: Acid leaching of P from partially/fully dried sewage sludge (PULSE) 122

3.4.1 Preparation of I3 .... *122*

3.4.2 Execution of I3 .... *146*

3.4.3 Analyses of results of I3 operation *154*

3.4.4 Discussion of results for I3 operation *158*

3.4.5 Conclusion for I3 .... *159*

4 Demonstration of solutions combining phosphorus removal and recovery 161

4.1 Demonstrator I4: Microalgae to recover P from small-scale WWTPs 161

4.1.1 Preparation of I4 .... *163*

4.1.2 Execution of I4 .... *173*

4.1.3 Analyses of results of I4 operation *174*

4.1.4 Discussion of results for I4 operation *183*

4.1.5 Conclusion for I4 .... *185*

4.2 Demonstrator I5: P adsorption for small scale use (FILTRAFLO™-P with CCM adsorbent) 186

4.2.1 Preparation of I5 .... *187*

4.2.2 Execution of I5 .... *198*

4.2.3 Analyses of results of I5 operation *205*

4.2.4 Discussion of results for I5 operation *208*

4.2.5 Conclusion for I5 .... *210*

4.3 Demonstrator I6.2: P precipitation at small-scale WWTPs (downscaled Struvia™) 211

4.3.1 Preparation of I6.2 .... *211*

4.3.2 Execution of I6.2 .... *218*

4.3.3 Analyses of results of I6.2 operation *229*

4.3.4 Discussion of results for I6.2 operation *241*

4.3.5 Conclusion for I6.2 .... *242*

5 Life Cycle Assessment – Life Cycle Costs works 245

5.1 System expansion methodology 247

5.1.1 Methodological choices *247*

5.1.2 Results for four recovery processes *254*

5.1.3 Discussion of results for LCA with system expansion approach *276*

5.2 Avoided burden methodology 278

5.2.1 Methodological choices *278*

5.2.2 Results for four recovery processes ... 279
5.2.3 Discussion of results for LCA with avoided burden approach ... 306
5.3 LCC analysis ... 307
5.3.1 LCC analyses of EuPhoRe® process ... 308
5.4 Conclusion of LCA-LCC works ... 310
6 Outlook ... 311
References ... 314

Figures

Figure 2.1.1: Overview of demonstrators and activities included in work package T1 36

Figure 3.1.1: General scheme of “wet-chemical” P-recovery processes..43

Figure 3.1.2: Removal of the sewage sludge from the chamber filter press at the WWTP of the Emschergenossenschaft in Bottrop...45

Figure 3.1.3: Filling of the SSA samples into special silos at the WWTP of the Emschergenossenschaft in Bottrop...45

Figure 3.1.4: Incineration plant of Innovatherm GmbH in Lünen..46

Figure 3.1.5: Process scheme of REMONDIS TetraPhos® process 51

Figure 3.1.6: REMONDIS TetraPhos® pilot plant in Werdohl-Elverlingsen 54

Figure 3.1.7: Leaching rates for phosphorus obtained during the trials phases with the REMONDIS TetraPhos® process...55

Figure 3.1.8: Phosphorus balance obtained with the TetraPhos® process applied to SSA of Bottrop WWTP without coal conditioning 56

Figure 3.1.9: Synthetic gypsum produced by TetraPhos® process (crystallisation/separation step) 57

Figure 3.1.10: Exemplary pictures taken during the experiment (here after contact time in the settling phase of the sludge)..58

Figure 3.1.11: SSA residues produced by TetraPhos® process..59

Figure 3.1.12: Process scheme of Phos4Life™ 61

Figure 3.1.13: Experimental set up for leaching stage for the Phos4Life™ process 61

Figure 3.1.14: Experimental set up for Solvent extraction stage (Fe-extraction) 62

Figure 3.1.15: Experimental set up for Solvent extraction stage (H_3PO_4-extraction) 62

Figure 3.1.16: Process scheme of PARFORCE technology used in the lab-tests 65

Figure 3.1.17: Phosphorus balance obtained with the PARFORCE process applied to SSA of Bottrop WWTP without coal conditioning as well as blends with high and low industrial influence (see chapter above)...66

Figure 3.1.18: Phosphoric acid samples after evaporation (SSA#3 to #5 from left to right)............67

Figure 3.1.19: Road salt samples after drying (SSA/Sample#1 to #3 from left to right) 69

Figure 3.1.20: Process scheme of the PARFORCE technology during pilot demonstration.............71

Figure 3.1.21: Phosphorus balance obtained in the pilot-tests with the PARFORCE process applied to sample SSA#5...72

Figure 3.1.22: Phosphoric acid samples after evaporation (left: without Al-separation, right: after Al-separation)........73

Figure 3.1.23: Road salt samples after drying (left) and brine (right)........76

Figure 3.1.24: Outlook on technology implementation of the “wet-chemical” P-recovery processes considered in Phos4You........79

Figure 3.2.1: Schematic overview of the EuPhoRe® process........81

Figure 3.2.2 a and b: Sludge storage........83

Figure 3.2.3 a and b: Sludge hopper and screws........83

Figure 3.2.4 a and b: Drag chain conveyor........84

Figure 3.2.5 a and b: Conveyor belt and rotating cutter........84

Figure 3.2.6 a and b: Dosing of additives and air lock........85

Figure 3.2.7 a and b: Inside views of the rotary kiln........86

Figure 3.2.8: External isolation........86

Figure 3.2.9: SSA discharge at the EuPhoRe®-plant........87

Figure 3.2.10 a and b: Gas split (flue/exhaust gas) and one of the two incineration chambers......88

Figure 3.2.11 a and b: Inside view of the filter and view of the whole gas treatment system........89

Figure 3.2.12 a and b: EuPhoRe®-SSA quality........92

Figure 3.2.13: Dry matter development for 5 harvests of perennial ryegrass, comparing EGLV 3% and 6% as compared to TSP and zero control........94

Figure 3.2.14: Dry matter development for 5 harvests of perennial alfalfa, comparing EGLV 3% and 6% as compared to TSP and zero control........95

Figure 3.2.15: Pellets of EuPhoRe®-SSA and 2 different types of salt-solution........96

Figure 3.3.1: pH evolution and P dissolution in non-digested sludge (CPD: chemical P dissolution, BPD: biological P dissolution)........103

Figure 3.3.2: pH evolution and P dissolution in digested sludge (CPD: chemical P dissolution, BPD: biological P dissolution)........103

Figure 3.3.3: pH evolution and P dissolution in MS2 with different co-substrate (Cos1: modified starch, Cos2: Erythrol)........105

Figure 3.3.4: pH evolution and P dissolution in MS3 with different co-substrate (Cos1 : modified starch, Cos2: Erythrol)........106

Figure 3.3.5: Biochemical methanogenic potential of acidified sludge compared to initial sludge (FM: fresh matter)........109

Figure 3.3.6: Perimeter of implementation of the demonstrator in the Marquette-Lez-Lille WWTP 110

Figure 3.3.7: Scheme of demonstrator in Lille (left) and Tergnier (right); 111

Figure 3.3.8: Both sides of the demonstrator in each location, Lille and Tergnier 111

Figure 3.3.9: Phosphorus concentration (total and dissolved) on Lille demonstrator 113

Figure 3.3.10: Percentage of solubilisation of phosphorus (left axis) and final pH (right axis) on Lille demonstrator. 114

Figure 3.3.11: Mineral and metals to phosphorus ratios (molar). 114

Figure 3.3.12: Phosphorus concentration (total and dissolved) on Tergnier demonstrator after bio-acidification. 115

Figure 3.3.13: Dissolved minerals and cations on Tergnier demonstrator after bio-acidification. 116

Figure 3.3.14: P-product crystals after washing 117

Figure 3.3.15: Comparison between dark fermentation and bio-acidification on P dissolution and VFA production 120

Figure 3.3.16: Comparison between experimental and simulated data during semi-continuous bio-acidification/dark fermentation experiments on Tergnier sludge 121

Figure 3.4.1: PULSE-process scheme. 122

Figure 3.4.2: Cascaded option tree for sludge-input options 123

Figure 3.4.3: Speciation using the SLLE tool. Initial concentrations in [mol/L]: Fe3+: 0.0703, Al3+: 0.0203, HCl: varying, PO4-3: 0.348, Ca2+: 0.2, Fe2+ - 0.03. The dashed curves show the precipitation equilibrium 125

Figure 3.4.4: Texture of undigested dewatered sludge from Oupeye WWTP (A): 20 to 22 %DM & dried sludge (B): >97 %DM 127

Figure 3.4.5: P-leaching efficiency from DS. Sludge: Oupeye WWTP, S/L ratio: 0.25, leaching duration: 60 min, DM: >97 %, room temperature 128

Figure 3.4.6: Effect of leaching time and S/L (solid-to-liquid) ratio on P leaching efficiency. Sludge: Oupeye WWTP, DM: >97 %........ 129

Figure 3.4.7: Effect of drying mechanism on leaching of sludge. Sludge: Oupeye WWTP, DM: >97 %, S1 –- rapid convective air drying for 4 h, S2 – slow drying without air circulation for 72 h at 80 to100 °C, S3 – drying without air circulation for 24 h at 100 °C 130

Figure 3.4.8: Cascaded option-tree evaluation of the acid to be used for sludge leaching 131

Figure 3.4.9: Nutrients and metals leached from sludge with H_2SO_4 and HCl. Sludge: Oupeye WWTP, DM: >97 %, S/L: 0.25, leaching duration: 1 h 132

Figure 3.4.10: Extraction efficiency of metal from HCl at1 mol/L based leach liquor, diluent: Ketrul-D80, modifier for Alamine336: Exxal10, solvent concentration indicated in vol %, O/A phase ratio: 2 133

Figure 3.4.11: Cascaded option tree for the selection of extractants 134

Figure 3.4.12: Fitting of extraction constant log K_{ext} and stochiometric coefficient for extraction of Fe from HCl based leach liquor. Solvent: 10 vol-% Alamine 336 + 10 vol-% TBP + 3 vol-% Exxal 10 + 77 vol-% Ketrul D80 -, O/A phase ratio: 1 135

Figure 3.4.13: Degree of re-extraction of metals from spent extractant. Spent extractant; 10 vol-% Alamine 336 + 10 vol-% TBP + 3 vol-% Exxal 10 + 77 vol-% Ketrul D80, O/A phase ratio: 1 .. 136

Figure 3.4.14: Degree of stripping of metals from the spent solvent at different concentrations of Na2CO3. Spent extractant; 10 vol-% Alamine 336 + 10 vol-% TBP + 3 vol-% Exxal 10 + 77 vol-% Ketrul D80, O/A phase ratio: 1 137

Figure 3.4.15: Evaluation of phase separation and drop diameter for separation of organic and aqueous phase. Extractant; 10 vol-% Alamine 336 + 10 vol-% TBP + 3 vol-% Exxal 10 + 77 vol-% Ketrul D80, leach liquor: 1 mol/L HCl, O/A phase ratio: 2 137

Figure 3.4.16: Estimation of settler length 138

Figure 3.4.17: Precipitation of different components from extracted sludge leach liquor as a function of pH with 5 mol/L NaOH 140

Figure 3.4.18: Simulation of Ca and P precipitation using SLLE tool 140

Figure 3.4.19: Precipitation of different components from extracted sludge leach liquor as a function of pH with 25% $Ca(OH)_2$ slurry in PULSE process 141

Figure 3.4.20: PULSE demonstrator construction at ULiège 143

Figure 3.4.21: PULSE demonstrator: drying, crushing, leaching, precipitation, and filtration modules installed inside container 143

Figure 3.4.22: Mixer-settler equipment for solvent extraction. Installed inside the Chemical Engineering Hall of ULiège 144

Figure 3.4.23: 5 stage mixer-settler equipment for solvent extraction tests in PULSE demonstrator 144

Figure 3.4.24 Tanks used for leaching and precipitation in I3 demonstrator 145

Figure 3.4.25: Pressurized bag filtration module and filter bag of 25 µm 146

Figure 3.4.26: Comparison of P leaching efficiencies between SLLE tool, lab experiments and demonstrator tests using HCl acid 148

Figure 3.4.27: SLLE tool v/s demonstrator average degree of extraction of metals from German sludge liquor from a 2-stage counter-current operation at different O/A phase ratios 149

Figure 3.4.28: I3 PULSE demonstrator at Oupeye WWTP 150

Figure 3.4.29: Comparison of P leaching efficiencies between SLLE tool, lab experiments and demonstrator tests using HCl acid 151

Figure 3.4.30: SLLE tool v/s pilot trial average degree of extraction of metals from Oupeye sludge liquor from a 2-stage counter-current operation 151

Figure 3.4.31: Filter bag containing the filter cake (Picture: ULiege/Z.Shariff) 152

Figure 3.4.32: PULSE demonstrator trial at waste-water Development Centre of Scottish Water in Bo'ness 152

Figure 3.4.33: Comparison of P leaching efficiencies between SLLE tool, lab experiments and demonstrator tests using HCl acid 153

Figure 3.4.34: SLLE tool v/s pilot trial avg. degree of extraction of metals from Scottish sludge liquor from a 2-stage counter-current operation 154

Figure 3.4.35: PULSE product during demonstrator trial with German sludge 154

Figure 3.4.36: Granulation tests by Prayon S.A. on the PULSE product obtained from German sludge. A - during granulation; B - granulated product wet; C- granulated product dry....... 159

Figure 4.1.1: Loads of P to EU regional seas, by source (tonnes/year in 2014) 161

Figure 4.1.2: Set-up of the process control parameters tests 163

Figure 4.1.3: Changes in the cell concentration in the medium during incubation. Each point represents mean value from three replicate determinations with standard deviation........ 165

Figure 4.1.4: Removals of PO_4 in the medium during incubation, expressed as the ratio between the PO_4 concentrations in the media (C_x) and the initial PO_4 concentration (C_0). Each point represents mean value from three replicate determinations with standard deviation........ 166

Figure 4.1.5: Removals of PO_4 in the medium during incubation at different light intensities and different temperatures, expressed as the ratio between the PO_4 concentrations in the media (C_x) and the initial PO_4 concentration (C_0) 168

Figure 4.1.6: Changes in the cell concentration in the medium during incubation at different light intensities and different temperatures 169

Figure 4.1.7: Changes in NH_4 and PO_4 concentrations in the influent and effluent during the experiment. Each point represents mean value from three replicate determinations with standard deviation 171

Figure 4.1.8: Changes in NO_3, NH_4 and PO_4 concentrations in the influent and effluent during the experiment. Each point represents mean value from three replicate determinations with standard deviation 172

Figure 4.1.9: Greenskill Environmental Technology Ltd. 75L and 500L PBRs installed at the Wastewater Development Centre in Bo’ness 174

Figure 4.1.10: Greenskill Environmental Technology Ltd. 75L PBR implemented at the Wastewater Development Centre in Bo'ness 175

Figure 4.1.11: Treatment process configuration with 75L PBR 175

Figure 4.1.12: Changes in the optical density in 75L PBR from the 19th till the 25th of June 2019 177

Figure 4.1.13: PO_4 and NH_4 concentrations in the influent, tank and effluent during the trial in Bo'ness (75L PBR) 178

Figure 4.1.14: COD concentrations in the influent and effluent (75L PBR) 179

Figure 4.1.15: Greenskill Environmental Technology Ltd. 500L PBR implemented at the Wastewater Development Centre in Bo'ness 179

Figure 4.1.16: On the left, microalgae biomass concentration in the PBR. On the right, microalgae biomass sedimentation after 5 min without (1) and after the addition of 0.5g L^{-1} of NaOH (2) 181

Figure 4.1.17: PO_4 and NH_4 concentrations in the influent, tank and effluent during the trial in Bo'ness (500L PBR) 182

Figure 4.1.18: COD concentrations in the influent and effluent (500L PBR) 183

Figure 4.2.1: Contour and three-dimensional response surface plots regarding the effect of IR and activation temperature (a-b), IR and activation time (c-d) and activation temperature and activation time (e-f) on phosphorus adsorption 189

Figure 4.2.2: SEM micrographs of pristine crab carapace (bar lengths 10 μm and 3.33 μm; magnification × 1000 and × 3000) (a–b); optimised CCM adsorbent (bar lengths 14.3 μm and 10 μm; magnification × 700 and × 1000) (c–d); SEM micrographs with EDX spectra for pristine crab carapace (e–f); the optimised CCM adsorbent (note the additional potassium-K signal) (g–h) 190

Figure 4.2.3: Nitrogen adsorption/desorption isotherms and BET data of raw crab carapace and the CCM adsorbent after optimisation (a), XRPD patterns of raw crab carapace and the optimised CCM adsorbent (Note: * reflections associated with calcite) (b) and FTIR spectra of raw crab carapace and the optimised CCM adsorbent (c) (experimental conditions: impregnation ratio for KOH:carapace (g/g) 1:1; activation temperature 105 °C; activation time 150 min) 192

Figure 4.2.4: Batch adsorption experimental results: adsorption equilibrium data (a), adsorption reaction kinetics (b) and P desorption in water, using 0.5 M HCl and 2 % citric acid as eluents (c) (initial concentration: 1–50 mg P/L; no pH adjustment; contact time: 1-300 min; dose of adsorbent: 1 g/L; rotation speed: 150 rpm - Note: the data (n = 3) are represented as mean ± standard error) 195

Figure 4.2.5: Fixed-bed column adsorption experiments: effect of bed height (a), initial phosphate concentration (b) and flow rate (c) (initial concentration: 5-20 mg P/L; no pH adjustment; flow rate: 3.5-10.5 mL/min; bed height: 3-10 cm) 197

Figure 4.2.6: Scottish Water Horizons Development Centre at Bo'ness 199

Figure 4.2.7: FILTRAFLO^{TM}-P pilot reactor designed by Veolia (a), the CCM adsorbent developed by ERI (b) and the airlift supported self-backwashing system visible at the bottom and right side of the unit (c) 200

Figure 4.2.8: FILTRAFLO^{TM}-P pilot reactor valve system (a) and with the IBC tanks (b) 201

Figure 4.2.9: Wastewater circulation within the FILTRAFLO^{TM}-P pilot reactor 201

Figure 4.2.10: Schematic of the pilot test process run with FILTRAFLO™-P unit and CCM adsorbent 202

Figure 4.2.11: P theoretical breakthrough curves (Bohart-Adams with solid line; Clark with dash line) for the field trials. Low P concentration influents (a) and high concentration influents (b) (0.5 mg P/L being the EU Water Framework Directive (WFD) and US National Pollution Discharge Elimination System (NPDES) regulation limit for sensitive water bodies and the 2 mg P/L point the common effluent limit EU member states need to meet depending on population equivalence and the presence of sensitive areas).. 205

Figure 4.2.12: The ratio between effluent and influent levels (C_e/C_i) for pH (a), conductivity (b) and turbidity (c) during the trials 206

Figure 4.2.13: Organic compound and nutrient removal efficiency during the trials (a-d) 207

Figure 4.2.14: Macro- and micro-element removal efficiency during the trials (a-d) 208

Figure 4.3.1: Macroom Wastewater Treatment Plant Schematic Diagram..................................... 213

Figure 4.3.2: Struvia™ process crystallisation reactor with TurboMix™, and lamella settlers....... 214

Figure 4.3.3: Jar test apparatus 215

Figure 4.3.4: Phosphorus precipitation in a jar test glass beaker 216

Figure 4.3.5: Struvia™ pilot plant container 219

Figure 4.3.6: Internal view of the Struvia™ pilot plant container 219

Figure 4.3.7: Struvia™ pilot plant service hatch 220

Figure 4.3.8: Struvia™ pilot plant layout 221

Figure 4.3.9: Simplified Struvia™ pilot plant schematic 222

Figure 4.3.10: Computerised control station with automatic shut off system............................... 223

Figure 4.3.11: Process flowsheet for the Struvia™ pilot plant at the WWTP................................... 224

Figure 4.3.12: Components inside the Struvia™ pilot plant 225

Figure 4.3.13: Recovered P product from the pilot plant at the WWTP 227

Figure 4.3.14: Establishment of the fluidized bed in the reactor 231

Figure 4.3.15: Change in phosphorus concentration during operation of the Struvia™ pilot plant starting the 19th of February 2020 232

Figure 4.3.16: Change in total nitrogen concentration during operation of the Struvia™ pilot plant starting the 19th of February 2020 233

Figure 4.3.17: Change in COD during operation of the Struvia™ pilot plant starting the 19th of February 2020 234

Figure 4.3.18: Change in alkalinity during operation of the Struvia™ pilot plant starting the 19th of February 2020 235

Figure 4.3.19: PO_4^{3-} removal at pH 10.6, 10.4 and 10.0 testing started 26th of November 2020 .. 236

Figure 4.3.20: Lime usage verse sludge production starting the 19th of February 2020 237

Figure 4.3.21: Water usage measurement started on the 24th of November 2020 239

Figure 4.3.22: P removal using recycled calcium products with additional pH adjustment 240

Figure 4.3.23: Incremental gypsum inclusion at 0.199 g/jar, with initial PO_4^{3-} concentration of 4.5 mg/L 241

Figure 4.3.1: System expansion vs. avoided burden 246

Figure 5.1.1: Flowsheet of the Oupeye WWTP 248

Figure 5.1.2: Results of the normalisation of the reference system impacts of the expansion system method: ReCiPe 2016 Midpoint (H) V1.04 / World (2010) H / Normalisation / Excluding long-term emissions 253

Figure 5.1.3: Boundaries for the reference system: 100 m³ of wastewater treated in the WWTP and 0.80 kg of P_2O_5 by chemical route 255

Figure 5.1.4: Environmental impacts of the multifunctional system including 100 m³ of treated water in the WWTP, and 0,80 kg of chemical P_2O_5 – Characterisation ReCiPe 2016 H/World H 256

Figure 5.1.5: System boundaries for the EuPhoRe® process in the multifunctional system 258

Figure 5.1.6: Environmental impacts of the multifunctional system including 100 m³ of treated water in the WWTP, the P recovery from the sewage sludge in EuPhoRe® process and the additional production of chemical P to obtain 0,80 kg of P_2O_5 – Characterisation ReCiPe 2016 H/World H 259

Figure 5.1.7: Environmental impacts of the production of 1 kg of P_2O_5 by EuPhoRe® process – Characterisation ReCiPe 2016 H/World H 260

Figure 5.1.8: Comparison of the EuPhoRe® system and the reference system in terms of environmental performance– Characterisation ReCiPe 2016 H/World H 261

Figure 5.1.9: Tergnier pilot plant of the Struvia™ process – the OPALIX part is not installed 263

Figure 5.1.10: System boundaries for the Struvia™ process in the multifunctional system 264

Figure 5.1.11: Environmental impacts of the multifunctional system including 100 m³ of treated water in the WWTP, the P recovery from the sewage sludge in Struvia™ process and the additional production of chemical P to obtain 0.80 kg of P_2O_5– Characterisation ReCiPe 2016 H/World H 265

Figure 5.1.12: Environmental impacts of the production of 1 kg of P_2O_5 by Struvia™ process– Characterisation ReCiPe 2016 H/World H 266

Figure 5.1.13: Comparison of the environmental impacts of the Struvia™ system and the reference system– Characterisation ReCiPe 2016 H/World H 267

Figure 5.1.14: System boundaries for the PARFORCE process in the multifunctional system 268

Figure 5.1.15: Environmental impacts of the multifunctional system including 100 m³ of treated water in the WWTP, the P recovery from the sewage sludge in PARFORCE process and the additional production of chemical P to obtain 0.80 kg of P_2O_5– Characterisation ReCiPe 2016 H/World H 269

Figure 5.1.16: Environmental impacts of the production of 1 kg of H_3PO_4 by PARFORCE process– Characterisation ReCiPe 2016 H/World H 270

Figure 5.1.17: Comparison of the environmental impacts of producing 1 kg of H_3PO_4 by conventional production and by the PARFORCE process– Characterisation ReCiPe 2016 H/World H 271

Figure 5.1.18: Comparison of the environmental impacts of the PARFORCE system and the reference system– Characterisation ReCiPe 2016 H/World H 272

Figure 5.1.19: System boundaries for the PULSE process in the multifunctional system 273

Figure 5.1.20: Environmental impacts of the multifunctional system including 100 m³ of treated water in the WWTP, the P recovery from the sewage sludge in PULSE process and the additional production of chemical P to obtain 0.80 kg of P_2O_5– Characterisation ReCiPe 2016 H/World H 274

Figure 5.1.21: Environmental impacts of the production of 1 kg of P_2O_5 by PULSE process– Characterisation ReCiPe 2016 H/World H 275

Figure 5.1.22: Comparison of the environmental impacts of the PULSE system and the reference system– Characterisation ReCiPe 2016 H/World H 276

Figure 5.2.1: System boundaries for the reference case with the avoided burden approach...... 280

Figure 5.2.2: Environmental impacts of the reference case with the avoided burden approach– Characterisation ReCiPe 2016 H/World H 281

Figure 5.2.3: System boundaries for the EuPhoRe® system with the avoided burden approach 282

Figure 5.2.4: Environmental impacts of the EuPhoRe® system with the avoided burden approach– Characterisation ReCiPe 2016 H/World H 283

Figure 5.2.5: Comparison of the environmental impacts of the EuPhoRe® system and the reference system with the avoided burden method – Characterisation ReCiPe 2016 H/World H........ 284

Figure 5.2.6: Comparison of the environmental impacts of the EuPhoRe® system for the three electricity mixes studied (German, Belgian and French) – Characterisation ReCiPe 2016 H/World H........ 285

Figure 5.2.7: Comparison of the environmental impacts of the EuPhoRe® system for the three levels of P_2O_5 content of the SSA studied (16 %: reference, 11.2 %: down and 20.8 %: up)– Characterisation ReCiPe 2016 H/World H 287

Figure 5.2.8: System boundaries for the PARFORCE system with the avoided burden approach 288

Figure 5.2.9: Environmental impacts of the PARFORCE system with the avoided burden approach– Characterisation ReCiPe 2016 H/World H 289

Figure 5.2.10: Comparison of the environmental impacts of the PARFORCE system and the reference system with the avoided burden method – Characterisation ReCiPe 2016 H/World H........ 290

Figure 5.2.11: Comparison of the environmental impacts of the PARFORCE system for the three electricity mixes studied (German, Belgian and French) – Characterisation ReCiPe 2016 H/World H........ 292

Figure 5.2.12: Comparison of the environmental impacts of the PARFORCE system for the two levels of P_2O_5 content in the digested sludge studied – Characterisation ReCiPe 2016 H/World H........ 293

Figure 5.2.13: System boundaries for the Struvia system with the avoided burden approach ... 295

Figure 5.2.14: Environmental impacts of the Struvia™ system with the avoided burden approach – Characterisation ReCiPe 2016 H/World H 296

Figure 5.2.15: Comparison of the environmental impacts of the Struvia™ system and the reference system with the avoided burden method – Characterisation ReCiPe 2016 H/World H........ 297

Figure 5.2.16: Comparison of the environmental impacts of the Struvia system for the three electricity mixes studied (German, Belgian and French)– Characterisation ReCiPe 2016 H/World H........ 298

Figure 5.2.17: Comparison of the environmental impacts of the Struvia™ system for the three levels of P_2O_5 content studied in the sludge – Characterisation ReCiPe 2016 H/World H 299

Figure 5.2.18: System boundaries for the Pulse system with the avoided burden approach 301

Figure 5.2.19: Environmental impacts of the PULSE system with the avoided burden approach – Characterisation ReCiPe 2016 H/World H 302

Figure 5.2.20: Comparison of the environmental impacts of the PULSE system and the reference system with the avoided burden method – Characterisation ReCiPe 2016 H/World H 303

Figure 5.2.21: Comparison of the environmental impacts of the PULSE system for the three electricity mixes studied (German, Belgian and French) – Characterisation ReCiPe 2016 H/World H 304

Figure 5.2.22: Comparison of the environmental impacts of the PULSE system for the three levels of P_2O_5 content studied in the sludge – Characterisation ReCiPe 2016 H/World H 305

Figure 5.3.1: Illustration of the principle of life cycle costing as applied to P-recovery technologies 307

Figure 5.3.2: Repartition of costs for EuPhoRe® process 309

Tables

Table 2.2.1: Key data of the Phos4You demonstrators 38

Table 3.1.1: Overview of the investigated “wet-chemical” P-recovery processes investigated 43

Table 3.1.2: Overview of the generated SSA samples 46

Table 3.1.3: SSIPs and mixing ratio of the different SSA samples 47

Table 3.1.4: Composition of the investigated SSA samples compared with usual values of purely municipal SSA from German SSIPs 48

Table 3.1.5: Overview of SSA samples used in the Lab- and Pilot-tests with different technologies 50

Table 3.1.6: Quality of REPACID® (converted to 75 % H_3PO_4) produced compared to product specifications 56

Table 3.1.7: Leaching rates for main compounds of different samples, achieved with the PARFORCE process 65

Table 3.1.8: Overview of the ingredients of the produced phosphoric acid samples converted to 75 % H_3PO_4 68

Table 3.1.9: Overview of the ingredients of the produced metal salt 69

Table 3.1.10: Overview of the ingredients of the produced road salt in comparison with the limit values on DIN EN 16811-2 70

Table 3.1.11: Leaching rates for main compounds of used samples SSA#5 compared to the results from the lab-tests, achieved with the PARFORCE process 72

Table 3.1.12: Overview of the ingredients of the produced phosphoric acid samples of used SSA samples#5 compared to the results from the lab-tests converted to 75 wt % H_3PO_4 74

Table 3.1.13: Overview of the ingredients of the produced metal salt solutions 75

Table 3.1.14: Overview of the ingredients of the produced road salt compared to the results from the lab-tests and the limit values on DIN EN 16811-2 76

Table 3.2.1: Phosphate solubility of lab-scale trials 82

Table 3.2.2: Average composition of sewage sludge of DO-Deusen (main elements) 91

Table 3.2.3: Average composition of sewage sludge of DO-Deusen (heavy metals) 91

Table 3.2.4: Overview on selected results of the SSA analyses (focussing on heavy metals) 92

Table 3.2.5: Overview on selected results of the SSA analyses (focussing on nutrients) 93

Table 3.3.1: Sludge characteristics within the BPDP test (TS: total solid, MS: mineral solid) 99

Table 3.3.2: Characteristics of the mixture used for the acidification test 99

Table 3.3.3: Concentrations after acidification (concentrations of total and dissolved phosphorus are in mg.l^{-1}) 100

Table 3.3.4: Recovery of each element in the liquid phase (%). (C= control) 101

Table 3.3.5: Final concentration in liquid fraction after bio-acidification (in mM) 101

Table 3.3.6: Characteristics of sludge used for the second bio-acidification experiment (raw matter basis) 102

Table 3.3.7: Amount of acidification agent required to reach pH = 4±0,5 102

Table 3.3.8: Fraction of total Iron in liquid after biological (BPDP) or chemical (CPD) acidification at different pH level. Data expressed in %. 104

Table 3.3.9: Characteristics of the sludge used for the bio-acidification (raw matter basis)........ 105

Table 3.3.10: Characteristics of the sludge used for the bio-acidification with Cos3 (raw matter basis) 106

Table 3.3.11: Characteristics of the resins tested........ 107

Table 3.3.12: Cations removal by the resins (% of the initial concentration) 107

Table 3.3.13: Sequence of tests carried out in Lille. 112

Table 3.3.14: IN/OUT balance of the STRUVIA™ process. 116

Table 3.3.15: Economic balance. 118

Table 3.4.1: Concentration of components in sludge leach liquor from Oupeye sludge before and after extraction. Leaching acid conc. 2 mol/L HCl; extraction with 10 vol% Alamine 336 + 10 vol% TBP + 3vol% Exxal 10 in Ketrul D80; extraction stages: 2; O/A phase ratio: 1 139

Table 3.4.2: Composition of different intermediate streams of the I3 demonstrator during operation with German sludge........ 155

Table 3.4.3: Composition of different intermediate streams of the I3 demonstrator during operation with Scottish sludge 156

Table 3.4.4: Composition of different intermediate streams of the I3 demonstrator during operation with Scottish sludge 157

Table 4.1.1: Characteristics of small scale WWTP's wastewaters used to evaluate the behaviour of the microalgae 170

Table 4.2.1: Varying operation conditions (bed height, flow and initial P concentration) and the results obtained for the fixed bed column experiments 198

Table 4.2.2: Typical composition of the secondary wastewater effluent used to test the FILTRAFLO™-P unit with CCM adsorbent 204

Table 4.3.1: Results of the jar test experiment using synthetic waste. 215

Table 4.3.2: Results of the jar test experiment using treated effluent from the WWTP 217

Table 4.3.3: Container specifications with the Struvia™ unit 218

Table 4.3.4: Influent and effluent samples analysis for the pilot plant in stage 1 230

Table 4.3.5: Summary of results at pH 10.8 243

Table 5.1.1: Scenarios for the multifunctional systems... 251

Table 5.2.1: Sensitivity analysis of the environmental impacts of the EuPhoRe® system for the three electricity mixes studied (German, Belgian and French) 285

Table 5.2.2: Sensitivity analysis of the environmental impacts of the EuPhoRe® system for the three levels of P_2O_5 content studied (16%: reference, 11.2%: down and 20.8%: up)............ 287

Table 5.2.3: Sensitivity analysis of the environmental impacts of the PARFORCE system for the three electricity mixes studied (German, Belgian and French) 292

Table 5.2.4: Sensitivity analysis of the environmental impacts of the PARFORCE system for a +30% variation P_2O_5 content in sludge 294

Table 5.2.5: Sensitivity analysis of the environmental impacts of the Struvia™ system for the three electricity mixes studied (German, Belgian and French).. 298

Table 5.2.6: Sensitivity analysis of the environmental impacts of the Struvia™ system for the three levels of phosphorus content studied 300

Table 5.2.7: Sensitivity analysis of the environmental impacts of the PULSE system for the three electricity mixes studied (German, Belgian and French).. 304

Table 5.2.8: Sensitivity analysis of the environmental impacts of the PULSE system for the three levels of P_2O_5 content studied in the sludge.. 306

Table 5.3.1: Financial data for the EuPhoRe® process 308

1 Introduction

The addition of phosphate rock to the list of critical raw materials for the European Union in 2014 renewed in 2017 and 2020 (European Commission 2014, 2017a, 2020a) underlines the need to increase the recycling rates of phosphorus materials in the EU. Given the non-substitutability of phosphorus in parallel to its essentiality for all living organisms, plus the lack of resources in the EU, a reliable access to phosphorus is a concern for European citizens. Fostering the uptake of innovations to recover phosphorus from different waste streams can alleviate Europe´s reliance on P-imports.

Municipal wastewater is one of the waste streams where phosphorus (P) can be recovered from. Empowering the stakeholders of the wastewater sector to gather experiences with P-recovery processes and to interact with European industries and stakeholders using P in their value chains would dramatically improve the likelihood of implementing the recycling of phosphorus from wastewater.

In support of the deployment of P-recycling, the Phos4You partnership conducted works to understand the drivers of the implementation of phosphorus recovery processes under real-life conditions. Twelve partners from seven countries cooperated to demonstrate and test innovative P-recovery technologies in the North-West Europe area.

1.1 Background of technical phosphorus recovery in North-West Europe

Wastewater treatment plants operators in North-West Europe will face new compliance requirements in the field of phosphorus removal and recovery in the near future.

Countries such as Switzerland or Germany have introduced in their legislations (Abfallverordnung, Schweizerischer Bundesrat 4/12/2015; AbfKlärV, Deutscher Bundestag 2017) a mandatory recovery of phosphorus from wastewater respectively from 2026 and 2029/2032 on (the deadline for implementation is depending on the size of the wastewater treatment plants (WWTP)). At the EU level, with the adoption of the Circular Economy Action Plan on March 2020 (European Commission 2020b), the Commission is committed to consider the revision of the Sewage Sludge Directive 86/278/EEC. The direct use of sludge in agriculture (as it is rich in nutrients such as nitrogen and phosphorus and it is a source of organic matter) is evaluated with regard of its contaminants level and its potential risk of pollution of soil, water and/or air (European Commission 2020d). In this context, one of the challenges that the project investigated is to understand the drivers for the implementation and the deployment of sustainable technical P-recovery facilities within existing infrastructures for wastewater treatment and sludge disposal.

In other countries, such as in Scotland, mitigation measures to reduce the P discharges from onsite wastewater treatment systems (OWTS) are required where there is a great potential to degrade ecological water quality (O´Keeffe et al. n.d. [2015]). At the overall EU level, small agglomerations, non-connected dwellings, individual or other appropriate systems were identified as remaining sources of loads having a significant pressure on the EU´s surface water bodies within the evaluation of the Urban Wastewater Treatment Directive (European Commission 2019). Design solutions integrating the recyclability of the removed phosphorus at small-scale WWTPs is a further challenge that the project investigated.

To support stakeholders of the wastewater sector selecting a P-recovery technology and developing a P-recovery strategy, Phos4You tackled the need for more demonstrations in real environment (EU COM - DG Research and Innovation 2015). The partnership made use of promising P-recovery processes, so far developed at lab or pilot scale, to upscale and/or test them in larger demonstrators operated under real-life conditions.

The Phos4You project brought together an interdisciplinary team including operators of WWTPs and sewage sludge incineration plants, process-holders, universities and research institutions to cooperate in the field of P-recycling. Fertilisers' manufacturers as well as national authorities and phosphorus or nutrients platforms were associated to the project, to permanently ensure that the recovery efforts fit with the numerous requirements of the users in different national contexts.

1.2 Objectives of a network of demonstrators

The objective of setting up a network of demonstrators was to demonstrate that the recovery of phosphorus is technically feasible, at different stages of the wastewater treatment and for different sizes of WWTPs throughout North-West Europe (NWE). One of the challenges of P-recovery at the beginning of the project is the lack of experiences in real environment with P-recovery processes as well as a high disparity between the NWE countries in regard with the handling of phosphorus discharged to WWTPs.

Successful experiences made with the demonstrators will enable WWTP operators to prepare their business plans towards an improved sustainable management of the phosphorus resource. It will also contribute to bring P-recovery related innovations closer to the market. To enable the full-scale implementation of P-recovery, it is necessary to gain experiences in real environment with existing innovative technologies and to further develop them. Furthermore, to facilitate the uptake of P-recovery technologies in the different territories in NWE, the network of demonstrators relies on the transfer of technology, knowledge and expertise between stakeholders.

The operation of the P-recovery demonstrators is used to:

- test the suitability of different input materials for each process;
- optimise existing processes;
- generate recovered P-materials of which quality will be assessed and of which integration in value chains will be evaluated or tested;
- support the development of models to enable the prediction of recovery efficiency with new inputs;
- provide reliable data to prepare business plans for P-recycling in urban or rural areas.

Successful implementation of the demonstrators has also further advanced the capability of wastewater treatment works operators, research institutes and universities to act in the field of P-recovery.

1.3 Scope of document

This report documents the works achieved within the project lifetime of Phos4You to make the proof of concept of seven solutions to recover phosphorus from wastewater. It also gives focus on the realised Life Cycle Assessment (LCA) and Life Cycle Costing (LCC) works.

Specifically, the following aspects of the project are discussed for each technical demonstration:

- *Preparation* of the demonstration, focusing on the preparatory works and results realised at labs (tests, experimentation);
- *Execution* of the demonstration, including the timeframe and locations of the operation, as well as the experimental set up;
- *Analyses* of the results of the operation of the demonstrators, including a dedicated part for the LCA and LCC aspects in chapter 5;
- *Discussion* of the results;
- *Conclusion* for the demonstrator.

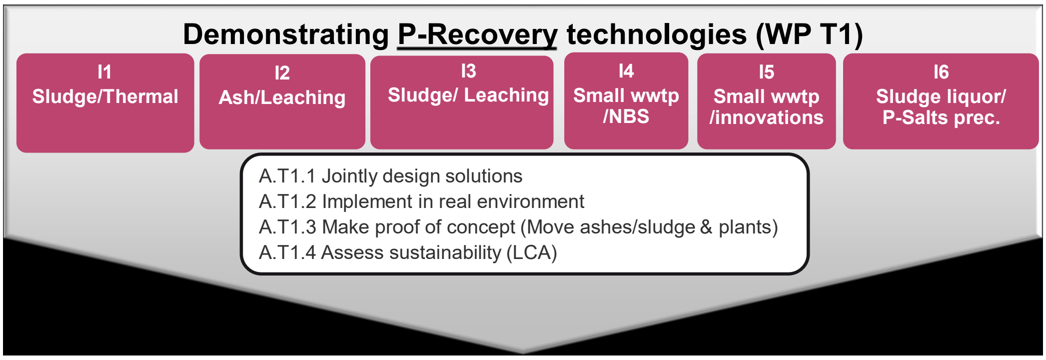
The term of “product” has been used to described the materials coming out of the processes. It doesn’t necessarily match with the definition of “product” in legal texts.

2 Overall set up of the network of demonstrators

2.1 Overview of the work package dedicated to P-recovery technologies

The work package on technical implementation of recovery processes (WP T1) was carried out over a four and a half years period, roughly from mid-2017 to mid-2021.

Figure 2.1.1 gives the overview of the demonstrators and activities included in the work package WP T1 "demonstrating P-recovery technologies".



P:Phosphor WP: Work Package T: Technical A: Activity I: Investment NBS: Nature Based Solutions

Figure 2.1.1: Overview of demonstrators and activities included in work package T1 (Ploteau 2016, modified)

In this technical work package six processes to recover phosphorus from wastewater were looked at. Based on existing research findings, the partners further developed and adjusted the various processes thanks to lab experimentations. They designed the plans of the demonstrators and obtained the necessary authorisations to run the network of seven demonstrators (for one process, two applications were demonstrated). Once set up at different locations, partners started to make the proof of the concepts by operating the demonstrators in real environment. Some of the demonstrators were moved to several locations or run with input materials of the several partners.

2.2 Selection of the demonstrated technologies

The selection of the processes has looked to ensure on one hand the demonstration of a wide range of input sources for the recovery of phosphorus (sewage sludge ashes, sewage sludge, sewage sludge liquor, wastewater effluent). On the other hand, the synergies that can arise between phosphorus removal and recovery for small scale wastewater treatment plants have been in focus.

Phos4You has demonstrated how phosphorus can be recovered (Figure 2.1.1):

- from sewage sludge with a thermochemical treatment (I1 – EuPhoRe® process);
- from sewage sludge with precipitation after a chemical leaching (I3 – PULSE process);
- from sewage sludge or liquor with crystallisation after a biological acidification (I6.1 – STRUVIA™ optimised with bio-acidification);
- from sewage sludge ashes with a leaching process (I2 – TetraPhos® process).

In addition, Phos4You has demonstrated how complementarity between phosphorus removal and phosphorus recovery can be achieved:

- from wastewater at small scale wastewater treatment works with nature based solutions (I4 – Microalgae *Chlamydomonas acidophila*);
- from wastewater effluent of smallest scale wastewater treatment works with adsorption filter using innovative adsorbents (I5 – Filtraflo™-P with chitosan-calcite adsorbent from seafood waste)
- from wastewater effluent of small scale wastewater treatment works with crystallisation process (I6.2 – STRUVIA™ downscaled)

Seven demonstrators have been developed, set up and operated within Phos4You.

Table 2.2.1 presents key data of the different demonstrators.

Table 2.2.1: Key data of the Phos4You demonstrators

ID	Input material	Process name	Principle	Recovery rate	Location (main phase)	Responsible partner	Capacity range (PE)	Operation timeframe
I1	Sewage sludge	**EuPhoRe®**	Thermochemical sewage sludge treatment	90 – 98 %	Germany	Emscherge-nossenschaft – EuPhoRe GmbH	3850 PE	2019 Aug - 2021
I2	Sewages sludge ashes	**TetraPhos®, PARFORCE, Phos4Life™**	Leaching extraction from ssa	>80 %	Germany/ Spain	Lippeverband	2050 PE*	2018 Mar - 2021
I3	Sewage sludge	**PULSE**	Leaching extraction from sewage sludge	60 – 70 %	Belgium	Uliège	500 PE	2020 Aug - 2021
I6.1	Sewage sludge	**STRUVIA™ optimised with bio-acidification**	Biological acidification and precipitation	50 %	France	INRAE & Veolia	1000 PE	2019 Mar - 2020 Jan
I4	Wastewater	**Microalgae *Chlamydomonas acidophila***	Microalgae growth for P removal & recovery at small WWTP	50 – 75 %	UK/Scotland	GCU	5 PE	2018 Jul - 2019 Dec
I5	Wastewater	**Filtraflo™ P with chitosan-calcite adsorbent**	Adsorption/filtration using seafood by-product for decentral P removal at small WWTP	60 %	UK/Scotland	ERI - Veolia	10 PE	2020 Jan - 2020 Feb
I6.2	Wwtp effluent	**STRUVIA™**	Precipitation with CaP for decentral removal at small WWTP	50 %	Ireland	CIT - Veolia	22 PE	2019 Dec - 2020 Mar

*for REMONDIS Tetraphos® and PARFORCE processes

The chapters 3 and 4 present in detail the proof of concept of each technology demonstrated in Phos4You. The experimental details and findings are reported. The LCA-LCC approach carried out to improve the eco-design of the processes is included for the relevant demonstrators in chapter 5.

2.3 Selected LCA-LCC approach

Authors: Gaspard Chantrain, Sylvie Groslambert, Angélique Léonard (ULiège); Anders Nättorp (FHNW)

In addition to the technical analysis of the phosphorus recovery demonstrators, an assessment of their environmental performance is included in the project. This environmental analysis is done using the life cycle analysis method. The Life Cycle assessment conducted for each process aimed at improving the eco-design of the technology and to quantify its environmental impacts.

Life Cycle Assessment is ruled by the ISO 14040:2006 and ISO 14044:2006 standards. The four mandatory steps of this analysis are: goal and scope definition, inventory analysis, impact assessment, and interpretation.

The goal and scope have been defined in order to be the same for all the demonstrators. The goal is the assessment of the environmental impact of the phosphorus recovery as defined in the frame of the Phos4You project.

Regarding inventories of demonstrators, it is important to bear in mind that most of the demonstrators are at lab or small pilot scale. Even if some scale-up rules exist and can help to extrapolate the data, it is very difficult to rely on lab scale data to assess the potential environmental impact of a process. All energy data are usually over-estimated since an industrial process usually benefits of energy optimisation. Moreover, yields that can be obtained at lab scale are rarely achieved when the industrial process is concerned.

Since no reliable inventory can be established from lab scale demonstrators, only the environmental analyses of the EuPhoRe®, PARFORCE, PULSE and Struvia™ processes were carried out. For this purpose, specific data from demonstrators were used to model the environmental impacts of the demonstrators.

All environmental impacts are assessed with the ReCiPe 2016 method (Huijbregts et al. 2017) by selecting the most relevant impact categories and using the Simapro software.

Papers reviews show that sewage sludge is mainly considered as “waste-to-product” sludge. The “zero burden assumption” is frequently applied and sludge is seldom charged with an environmental burden associated with its production (cut-off approach). This is not questionable when sewage sludge is considered as “waste” or “waste-to-product” sludge with energy recovery. However, this is becoming more debatable when sludge is considered as “product” sludge or as “waste-to-product” sludge with nutrient or material recovery. In such cases, the “zero burden assumption” is a no longer valid hypothesis as the sludge life cycle needs to be fully considered. This can only be done if the sludge carries an upstream environmental burden (Pradel et al. 2016). This leads to the problem of allocating the environmental costs of the treatment plant between its two functions, the primary one which is wastewater treatment and the secondary one which is sewage sludge production. This difficulty can be tackled by several methodological approaches, a number of which have been studied in the framework of the project.

Initially, the system expansion approach has been applied to evaluate environmental impacts of the Euphore®, PARFORCE, PULSE and Struvia™ demonstrators, and to a reference scenario for comparison. This methodological approach considers the environmental impacts of sludge production by including the whole wastewater treatment plant in the system boundaries studied. The boundaries then include the wastewater treatment plant and the production of phosphorus fertiliser which implies that the whole system is multifunctional (wastewater treatment function coupled with phosphorus fertiliser production function). The functional unit of such a system include the treatment of the wastewater (100 m³) and the production of 0.80 kg of P_2O_5 fertiliser (from P recovery in Phos4You demonstrators and/or chemical route). The wastewater treatment was modelled by a large size Belgian WWTP (Liège-Oupeye). The treatment of 100 m³ of wastewater generates a certain amount of sludge, and its valorisation to recover P was realised using the Phos4You demonstrators. The valorisation of sewage sludge by the demonstrators produces a quantity of material rich in phosphorus lower than 0.80 kg of P_2O_5 and the complement to obtain the reference amount of 0.80 kg of P_2O_5 came from the "BAU" P fertiliser production route (chemical). The reference system consists in the co-incineration of the sewage sludge together with the chemical production of the totality of the P fertiliser.

In a second part of the project, the methodological approach has been reviewed and the “avoided burden” approach has been added. At this time, it was also decided to include sludge biodigestion as well as cogeneration with electricity and heat recovery in the studied scenarios, as this is state-of-the art e.g. in Germany. The reference scenario for sludge treatment is also changed to mono-incineration of digested sludge with energy recovery (heat and electricity).

The environmental performance of each demonstrator has been therefore studied with the two methodological approaches and compared with the performance of the reference system. A detailed environmental assessment of each process also has allowed to highlight the most impacting steps for each process and to formulate eco-design advices. Two sensitivity analyses have also been performed. The first one aimed at evaluating the influence of the location of the demonstrator (Germany, France or Belgium). The second sensitivity analysis has been performed to investigate the impact of phosphorus variation in the sewage sludge used on the environmental performance of the process.

Finally, a life cycle cost analysis of the fertilisers delivered by the demonstrators of the project has also been carried out to estimate the economic feasibility of these P-materials. The principle of this type of analysis applied to a demonstrator is to account for all monetary flows out of and into the system. This analysis could make it possible to estimate two useful values. The first is the production cost of phosphorus-rich materials (in €/kg P_2O_5) and the second is the cost of processing one tonne of sewage sludge through the demonstrator (in €/tonne of sewage sludge treated). These two parameters illustrate the two functions of the demonstrators; the first one being the production of P-materials and the second one the treatment of the sewage sludge.

3 Demonstration of phosphorus recovery solutions

Four solutions to recover recyclable phosphorus materials either from sewage sludge or from sewage sludge ashes are presented in this chapter.

3.1 Demonstrator I2: Acid extraction of P from SSA (REMONDIS TetraPhos®, PARFORCE, Phos4Life™)

Author: Dennis Blöhse, Issa Nafo (Lippeverband)

Phos4You demonstrated how phosphorus can be recovered from sewage sludge ashes (SSA) with a leaching process.

The Lippeverband (LV) has commissioned the investigation of three “wet-chemical” recovery processes within the framework of Phos4You. Details of the process providers, the main process differences and the scope of the investigations are summarized in Table 3.1.1.

There are a number of suppliers on the market for processes for “wet-chemical” P-recovery from SSA. A large part of the developed processes is aimed at the production of phosphoric acid, which is very versatile and, depending on its quality, can be used in the fertiliser industry but also for other industrial applications.

The procedures are all based on the same principle (Figure 3.1.1). First, the phosphates are dissolved from the SSA matrix using acid and the SSA residue is separated. Since many undesirable accompanying substances or impurities (including iron, aluminium and calcium as well as heavy metals) are also transferred to the solution (raw phosphoric acid), the next step is the separation of impurities. Finally, the purified phosphoric acid is brought to the usual market concentration by evaporation.

Differences between the processes lie in the use of different eluants (here phosphoric acid, sulfuric acid, hydrochloric acid or nitric acid), but especially in the process steps used for the separation of impurities, i.e. purification of the raw acid (eluate of the elution stage). Ion exchangers, solvent extraction and also electrodialysis are used here (Table 3.1.1). Furthermore, different by-products are generated during the separation of accompanying substances or impurities. These mainly include iron and aluminium salts as well as calcium compounds (Table 3.1.1).

Table 3.1.1: Overview of the investigated "wet-chemical" P-recovery processes investigated (Ploteau et al. 2020), modified/translated

Process	**TetraPhos®**	**PARFORCE**	**Phos4Life™**
Provider	REMONDIS Aqua Industrie GmbH & Co. KG	PARFORCE Engineering & Consulting GmbH	Técnicas Reunidas S.A.
	Differences between the processes		
Elution agent	H_3PO_4	HCl	H_2SO_4
Process steps for impurities removal	Gypsum crystallisation Ion exchanger	Solvent extraction Ion exchanger Electrodialysis	Solvent extraction
By-products	Gypsum, Fe-/Al-chloride	Fe-/Al-salt solution, brine or road salt	Metal concentrate, $FeCl_3$
	Scope of work		
Tests description	Lab-pretrials and pre-industrial demonstration	Lab-pretrials and pre-industrial demonstration	Lab-pretrials of relevant process steps
Processing time	02/2018 – 03/2019	12/2019 – 05/2020 02/2021 – 06/2021	01/2020 – 07/2020

Figure 3.1.1 shows the essential process steps and the basic procedure - but due to the complexity, internal process cycles are not shown. A detailed explanation of the process will be given in the corresponding sections.

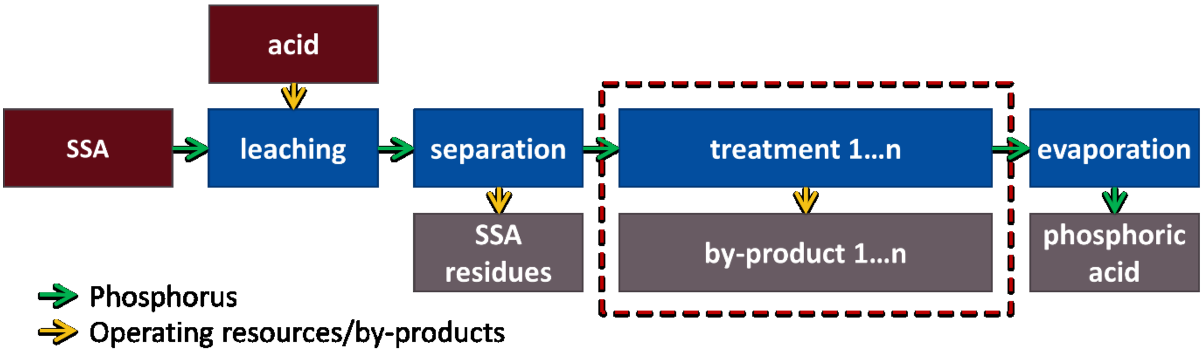


Figure 3.1.1: General scheme of "wet-chemical" P-recovery processes

Different SSA samples were tested during the investigations. The sample batches came from the incineration plant of Emschergenossenschaft (EG) in Bottrop and the Innovatherm GmbH in Lünen. In addition, samples from other incineration plants of the Wupperverband/SVA Buchenhofen (Wuppertal) and the WFA Elverlingsen GmbH (Werdohl) were used.

The focus of the investigations is not necessarily on a final process comparison, but rather on the combination of different experiences with external processes. Of particular interest here are the range of results with regard to chemical consumption, energy requirements (electricity, heat, steam), wastewater generation and the value-added chains in the recycling of the various by-products. Furthermore, the possible investment costs and space requirements can be estimated much better in case of industrial implementation.

3.1.1 Preparation of I2

Several tonnes of SSA were required for the investigations. The focus of the demonstration was the investigation of different SSA qualities. It was also of great interest to illustrate future changes in the SSA composition.

3.1.1.1 *Sampling of SSA from Bottrop/Lünen*

The Emschergenossenschaft operates a sewage sludge incineration plant (SSIP) in Bottrop, which is still being operated with coal-conditioned sewage sludge at the time of the trials. The conditioning with coal is on the one hand historically justified and on the other hand necessary in order to optimally adjust the dewatering properties and the calorific value of the sewage sludge.

In the future, the use of coal conditioning will be abandoned and instead the calorific value will be adjusted by solar-thermal drying of the sewage sludge. In addition to positive effects on the consumption of fossil resources, this also makes it necessary for the study to depict this considerable change in SSA composition.

Therefore, it was necessary to operate the SSIP in Bottrop in a special campaign with dewatered sewage sludge without coal conditioning. The biggest challenge for the operating staff was to dewater the sludge by means of the chamber filter presses. Because no coal was used, the sludge was very sticky and had to be removed manually from each individual chamber of the press (Figure 3.1.2).

Figure 3.1.2: Removal of the sewage sludge from the chamber filter press at the WWTP of the Emschergenossenschaft in Bottrop (Pictures: Emschergenossenschaft)

At the end of the campaign, two SSA samples could be produced in Bottrop for the investigations. They were filled into suitable silos for the demonstration (Figure 3.1.3).

Figure 3.1.3: Filling of the SSA samples into special silos at the WWTP of the Emschergenossenschaft in Bottrop (Pictures: Emschergenossenschaft/D. Blöhse)

In addition, several hundred kilograms of SSA sample from the SSIP of Innovatherm GmbH in Lünen were used for the investigations. Innovatherm GmbH in Lünen (Figure 3.1.4) is a subsidiary of BETREM GmbH, which in turn is a subsidiary of the Emschergenossenschaft and contributes widely to the safe disposal of sewage sludge from the LV and EG.

Since Innovatherm GmbH thermally uses a large proportion of sludge, including industrial sludge, in addition to EGLV's sewage sludge, the sample from this plant is considered as an SSA sample mainly from industrial sources, which is also reflected in its composition (see sections below).

Figure 3.1.4: Incineration plant of Innovatherm GmbH in Lünen (Pictures: Innovatherm GmbH/PUSCHELS.COM)

Table 3.1.2 provides an overview of the SSA samples generated in this first campaign 2018.

Table 3.1.2: Overview of the generated SSA samples

Sample ID	SSIP Location	Characteristics
SSA#1	Lünen (Innovatherm GmbH)	Real conditions
SSA#2	Bottrop (EG)	Real conditions
SSA#3	Bottrop (EG)	Modified conditions (without coal conditioning)

3.1.1.2 *SSA blends*

During the investigations different ashes were used. In the first demonstration of the TetraPhos® process two different SSA from SSIP Bottrop and one from SSIP Lünen were used (see previous section).

In the further course of the investigations, the SSA#3 sample of Bottrop was used as "reference ash". This was mixed with SSA from other SSIPs (Table 3.1.3) for further findings, so that a wide range of different SSA qualities could be tested.

Table 3.1.3: SSIPs and mixing ratio of the different SSA samples

Incineration-plants	**Bottrop** Emscher-genossenschaft	**Werdohl** WFA Elverlingsen GmbH	**Wuppertal** Wupperverband/ SVA Buchenhofen	**Lünen** Innovatherm GmbH
SSA#3 (reference)	100 %	-	-	-
SSA#4	24.2 %	19.9 %	8.4 %	47.5 %
SSA#5	44.7 %	37.2 %	18.1 %	-

By using SSA#1 (3.1.3.1) or adding (3.1.3.2 and 3.1.3.3) a sample batch from Innovatherm in Lünen in SSA#4, the influence of combustion ashes from sludge of industrial origin could be investigated. The main characteristic of these ashes is the comparatively low phosphorus content of 3 to 6 %. Further differences are explained in the following sections.

3.1.1.3 *Characterisation of the SSA samples used*

Table 3.1.4 shows the composition of the SSA used during the investigations. For comparison, the “average” values as well as “ranges” of values of purely municipal sewage sludges in Germany are listed (report monitoring German SSIPs in 2012 and 2013 (Krüger and Adam 2014). In general, the SSA used are characterised by the presence of low P contents and a high load of heavy metals.

Table 3.1.4: Composition of the investigated SSA samples compared with usual values of purely municipal SSA from German SSIPs (Krüger and Adam 2014), (REMONDIS Aqua Industrie GmbH & Co.KG. 2018), (REMONDIS Aqua Industrie GmbH & Co.KG. 2019), (PARFORCE Engineering & Consulting GmbH 2020), (PARFORCE Engineering & Consulting GmbH 2021)

Elements	Unit	sample ID					municipal SSA	
		SSA#1	SSA#2	SSA#3	SSA#4	SSA#5	average	range
P	%	**2.8**	**5.3**	**5.9**	**4.2**	**5.6**	9.2	**5.9**-13.1
Al		**4.5**	6	5.3	**4.3**	5.5	5	2.2-20.2
Ca		**13.1**	7.9	9.0	**12.2**	8.1	10	6.9-17.7
Fe		**8.6**	10	11.7	**9.7**	10.4	10.6	1.8-20.3
Mg		1.6	1.4	1.4	1.4	1.3	1.2	0.3-3.9
S		2.1	0.4	0.5	1.5	0.9	0.8	0.3-6.9
Si		11.6	N/A	15.2	10.8	14.2	12	4.4-20.7
As	ppm	**36.3**	**46**	**34.5**	**34.0**	**24.0**	**13.6**	4.2-124
Cd		**6.4**	1.6	**4.9**	**6.9**	**4.3**	**2.7**	0-14
Cr		**590**	N/A	**239**	**421**	**236**	**148**	79-1,088
Cu		**1,813**	**770**	**776**	**1,337**	**964**	**832**	225-2,477
Hg		0.3	1.2	0.6	0.3	0.3	0.5	0.1-3.6
Ni		**601**	**220**	**241**	**435**	**184**	**69**	8-**191**
Pb		**709**	**260**	**268**	**548**	**191**	**113**	54-**363**
U		2.6	4.8	4.7	3.4	4.0	6.3	2-25
Zn		**5,297**	**3,350**	**3,577**	**4,187**	**3,378**	**2,820**	844-**4,930**

The following characteristic properties can be derived from the comparison with purely municipal SSA (Table 3.1.4):

- Phosphorus is in part notably below the usual values (range).
- Nickel exceeds the usual values (range), in some cases notably.
- Arsenic, Cadmium, Chromium and Copper are notably above the average.
- Lead and Zinc are notably above average and exceed the usual values (range), in some cases notably.

As explained above, in the samples SSA#1 and SSA#4 the industrial influence compared to the other samples (SSA#2, 3 and 5) by increased lead and zinc and low P content is clearly shown. In addition, it can be seen that iron and aluminium are lower (less municipal sewage sludge), but the calcium content is increased (use of limed industrial sludge).

3.1.2 Execution of I2

In order to test the suitability of the SSAs of the Emscher-Lippe region to have its phosphorus recovered, three different leaching technologies were selected and applied to the SSA:

- The REMONDIS TetraPhos® technology,
- The Phos4Life™ technology,
- The PARFORCE technology.

The focus was primarily on processes that also promote the production of high-quality phosphoric acid as a product. The results should provide in-depth process knowledge and demonstrate the understanding of different approaches, especially for the purification of raw phosphoric acid, as well as the production and possible uses of various by-products. This offers the possibility for approaches for process optimisation as well as for the development of different business cases. A further reason for additional investigations existed particularly against the background of the scenarios to be considered "inter-communal cooperation", whereby it is of special interest to include SSA samples of neighbouring water management associations (here Ruhrverband and Wupperverband) in the investigations. This was not yet taken into account in the previous investigations using the REMONDIS TetraPhos® process.

The main differences between the processes or process steps used lie in the use of different eluants (here phosphoric acid, sulfuric acid, hydrochloric acid or nitric acid), but especially in the separation of impurities, i.e. the purification of the raw acid (eluate of the elution stage). In the TetraPhos® process tested in the first step, ion exchangers are used for the separation of impurities.

On the basis of market exploration, the PARFORCE and Phos4Life™ processes meet the desired technical limits compared to the REMONDIS TetraPhos® process with the aim of producing phosphoric acid. As process engineering variants, the purification is carried out by means of 1.) solvent extraction and 2.) electrodialysis. These possibilities are considered as process variants within the scope of the investigations.

Preliminary tests with all processes were carried out in the laboratory, depending on the possibility of mapping the processes on a laboratory scale in slightly different ways.

Essentially, the work included the following tasks: characterisation of the samples and preliminary leaching tests. In addition - depending on the possibility of mapping the process chain on a laboratory scale - preliminary tests were also carried out in part to remove impurities and in one case by-products and phosphoric acid were also produced.

The technologies were demonstrated on a pre-industrial scale using REMONDIS TetraPhos® and the PARFORCE process. Both technology providers have a corresponding pilot plant which guarantees further investigations.

Based on the knowledge gained from these laboratory tests, the investigations were continued on a pre-industrial scale. This made it possible to generate relevant data on the processes and to produce recovered materials and by-products in order to incorporate their quality and ability to be integrated into value chains into further investigations.

Basically, batch tests/continuous tests with several tonnes SSA were performed. Table 3.1.5 gives an overview of the SSA samples used in the different investigation orders.

Table 3.1.5: Overview of SSA samples used in the Lab- and Pilot-tests with different technologies

Technologie	Lab-tests	Pilot-tests
TetraPhos®	SSA#1, 2, 3	SSA#3, (1*)
Phos4Life™	SSA#3, 4, 5	-
PARFORCE	SSA#3, 4, 5	SSA#5

*just elution and separation step

The following test results as well as assessments of quality or usability and marketability are based on information provided by the technology suppliers (REMONDIS Aqua Industrie GmbH & Co.KG. 2018), (REMONDIS Aqua Industrie GmbH & Co.KG. 2019), (Técnicas Reunidas 2020), (PARFORCE Engineering & Consulting GmbH 2020, 2021) as well as investigations (Westfälisches Umwelt Zentrum 2020) and statements by third parties.

3.1.3 Analyses of results of I2 operations

3.1.3.1 *REMONDIS TetraPhos® process*

The results of the trials achieved with the REMONDIS TetraPhos® process are presented as already published within the European Conference Sludge Management 2019 (Blöhse and Herr 2019).

3.1.3.1.1 Process description

Leaching: The sewage sludge ash (SSA) is mixed with diluted phosphoric acid and dissolves practically all of the phosphates. The phosphoric acid used is removed from the product stream (Figure 3.1.5). This means that the process only requires an initial portion, after which the elution stage is operated with phosphoric acid produced in-house, thus reducing the need for externally supplied chemicals. Separation: After this elution stage, the insoluble material in the SSA (approx. 50 %) is filtered off (SSA residues). The filtrate is the crude phosphoric acid.

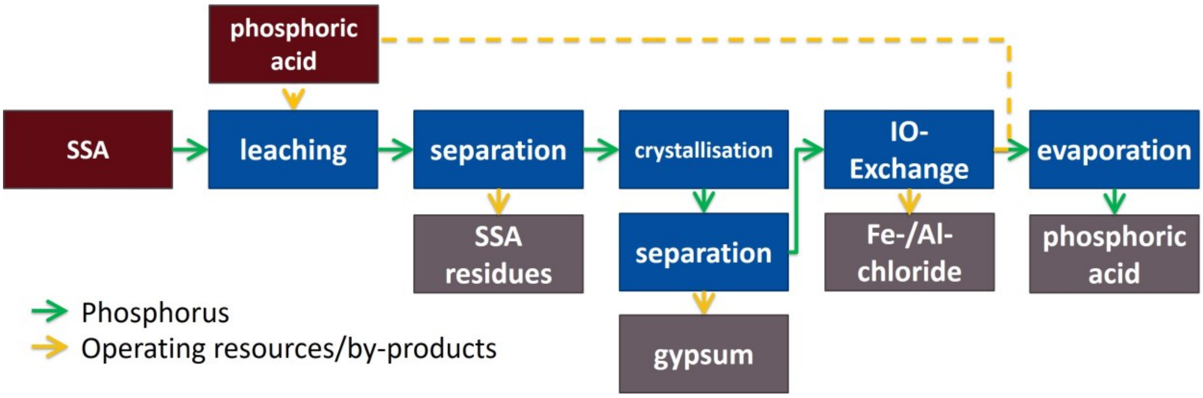


Figure 3.1.5: Process scheme of REMONDIS TetraPhos® process

Crystallisation/separation: The calcium that also dissolved from the SSA into acid (10-20 gCa/l acid) is then precipitated from crude phosphoric acid by adding a stoichiometric amount of sulfuric acid. This forms calcium sulfate, which is then filtered out of the phosphoric acid as gypsum. At the same time, the protolytic reaction of the H^+ions in the sulfuric acid forms phosphoric acid: $Ca(H_2PO_4)_2 + H_2SO_4 \rightarrow CaSO_4 + 2H_3PO_4$. In this respect, it is the H^+ions from sulfuric acid that are the real “active ingredient” that creates phosphoric acid (H_3PO_4) from the phosphate (PO_4^{3-}).

Ion-Exchange: The remaining metals, such as magnesium, aluminium and iron, are then removed using a very selective ion exchange resin. A metal salt solution is created by regenerating the ion exchangers with acids (HCl).

Evaporation: During the final phase, the phosphoric acid (now with low metal content) is concentrated to 75 %, in a vacuum evaporator.

The TetraPhos® process described generates an industrial quality phosphoric acid (trademark: REPACID®), which is suitable for use in industrial applications.

3.1.3.1.2 Pre-trials

Preliminary lab scale tests were conducted using SSAs with different phosphorus content (3-6 % P) to assess phosphorus extraction behaviour. In the pre-trials, three SSA (#1, 2, 3, Table 3.1.5) of varying quality were tested (Table 3.1.4).

The following objectives were pursued in the laboratory-scale preliminary tests:

- Selection of SSA quality for the subsequent demonstration tests from the three SSA samples provided;
- Identification of process parameters and operating settings for the selected SSA quality as a basis for the subsequent demonstration test;
- Characterisation of the various SSA samples in comparison with historical data (report monitoring german SSIPs in 2012 and 2013 (Krüger and Adam 2014) to determine if the available samples are representative for the SSIP;
- Investigation of effects due to coal-based sewage sludge conditioning practiced in Bottrop on the properties of the resulting SSA.

After characterising SSA samples as well as coal mixture used for sewage sludge conditioning in Bottrop, the process stage of elution in the TetraPhos® process was simulated with the SSAs on a laboratory scale. In addition to determining the phosphorus release (target: >80 % of phosphorus) the release of selected metals was considered as an important partial aspect. In addition, the filtration properties of the suspension of acid and SSA were of central importance. During the elution tests, the elution parameters were varied individually in order to determine the optimum parameter set for the respective sample.

Conclusions on the pre-trials

In order to check the filtration properties in advance, a particle size separation was also carried out. Here, no significant difference between the studied SSAs and no negative effect on the filtration process from particle size were identified.

In order to gain preliminary knowledge on the influence of coal conditioning, the incineration residue of black and brown coal was investigated. The following things were learned:

- The P content of coal SSA was below the detection limit;
- The coal conditioned SSA (SSA#2) carried a higher aluminium, sulfur, and magnesium content than the unconditioned SSA (SSA#3).

With all three SSAs, a successful elution investigation was conducted by varying different elution parameters. After optimising the specific parameter sets, the following results (REMONDIS Aqua Industrie GmbH & Co.KG. 2018) were obtained:

EGLV SSAs have a low phosphorus content compared to German municipal SSA. The influence of the higher portion of industrial wastewater of external industrial sludges especially in the sample from Lünen (SSA#1) is clearly recognisable. Typical mineral phases like whitlockite, quartz, hematite, and aluminium phosphate were identified. Calcium sulfate-anhydride was found in the SSA#1 sample.

- For all three SSAs, the future legal requirement of >80 % recovery of phosphorus will be met, and in some cases significantly exceeded.
- From a technical point of view, the coal conditioning is not a problem for the recovery of the resulting residue with the TetraPhos® process.
- From an economic point of view, the coal conditioning must be removed in order to prevent a reduction of P-content.
- The high industrial influence, especially in the SSA#1 from Lünen (lower P-content and higher Ca-content through external industrial sludges), is technically manageable but should be kept to a minimum to improve the profitability of the process.

Considering future changes to the EGLV sewage sludge strategy, it was decided to carry out a pre-industrial scale demonstration with the SSA from Bottrop without coal conditioning (SSA#3).

3.1.3.1.3 Pre-industrial demonstration

Following the lab scale tests, the TetraPhos® pilot plant (Figure 3.1.6) located in Werdohl-Elverlingsen (capacity 50-100 kg SSA/h) (Blöhse and Herr 2018) was operated for several months processing one EGLV SSA type. Operation of the demonstrator proved stability of the process with high and constant quality of the produced acid.

Figure 3.1.6: REMONDIS TetraPhos® pilot plant in Werdohl-Elverlingsen (Pictures: REMONDIS Aqua Industrie GmbH & Co.KG. /P. Herr)

It will be examined in particular whether the previously successfully tested process equipment (Blöhse et al. 2018; Rak 2018) is also suitable for the utilisation of EGLV SSA and whether the parameter set identified during lab pre-trials would also lead to successful results in large scale operation. Preliminary pre-industrial tests confirmed this, which lead to two key aspects to be demonstrated:

- A stable operational cycle that produces recycled phosphoric acid (REPACID®) that complies with all product specifications;
- An effective phosphorus recovery process with a P-recovery rate of >80 %, in accordance with future legal requirements.

Leaching rates

During the start-up phase of the facility and during the demonstrational operation, samples of SSA residue were tested at intervals for phosphorus content. It was shown that during the entire operation of the facility, the requirement for >80 % P-recovery was met.

The following Figure 3.1.7 shows the high efficiency of the elution step. In several campaigns it could be proven that the phosphorus leaching rate is consistently far above the required 80 %.

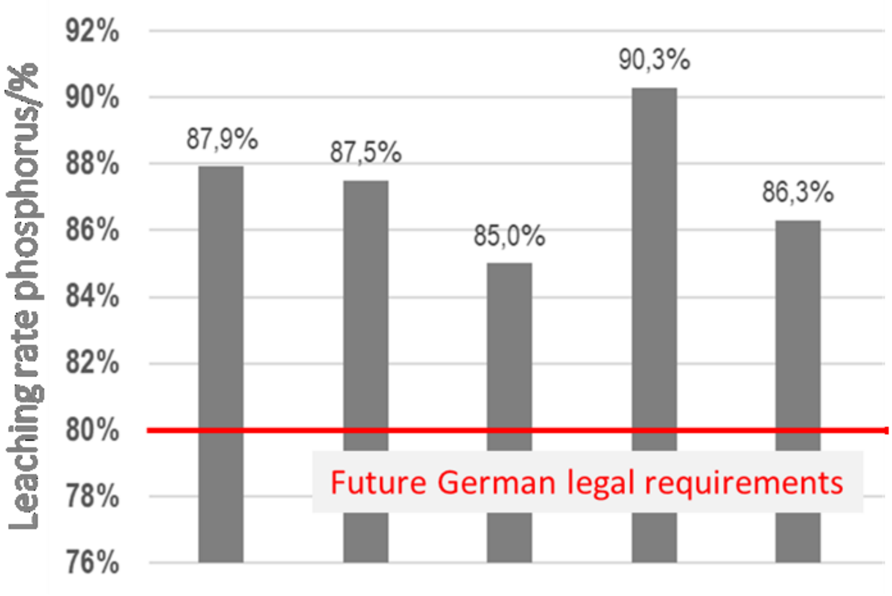


Figure 3.1.7: Leaching rates for phosphorus obtained during the trials phases with the REMONDIS TetraPhos® process (Herr 2018)

As listed above, other substances, such as calcium, iron and aluminium are also dissolved out of the SSA matrix. As mentioned above, these by-products can be removed from the system as by-product and fed into various value chains (see also following chapter).

Due to the use of a special precipitant, the elution rates of the heavy metals are very low. A large proportion of the heavy metals is incorporated into the SSA matrix and thus removed from the system in advance.

Phosphorus balance

From the results of the operational investigation (REMONDIS Aqua Industrie GmbH & Co.KG. 2019), a phosphorus balance was created over the recovery of sample SSA#3 through the TetraPhos® process, the results of which are displayed in Figure 3.1.8. For each of the process steps: Elution, Crystallisation, and Ion exchange, independent balances were created and then linked to the whole process. The evaporator step was not considered in the balance, because no phosphorus exits the system here.

The presented balance shows that the efficiency of the process in terms of phosphate recovery is very high. From the eluate (crude phosphoric acid to the marketable product

(REPACID®), only an additional 3.6 % of phosphorus is built into gypsum and recycled in metal salt (precipitation agent) by-products.

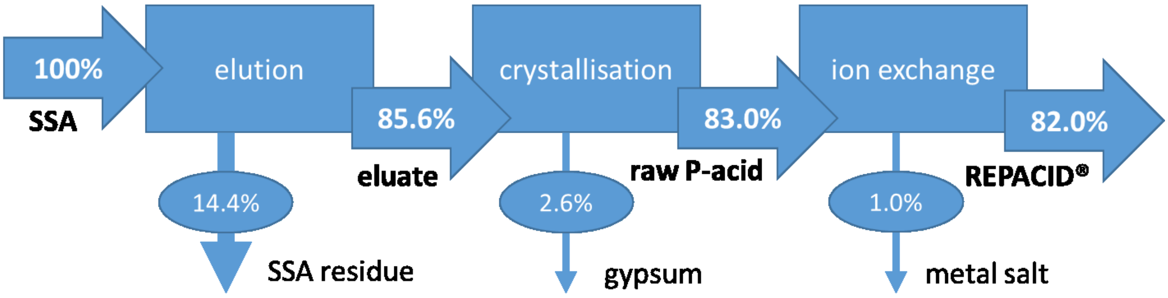


Figure 3.1.8: Phosphorus balance obtained with the TetraPhos® process applied to SSA of Bottrop WWTP without coal conditioning (Blöhse and Herr 2019)

Product quality

Phosphoric acid

The generated phosphoric acid REPACID® is of high quality with low impurities (Table 3.1.6) and is suitable for industrial applications. In all considered samples, the recovered phosphoric acid complies with the specifications of the product marketed under the trademark REPACID®.

Table 3.1.6: Quality of REPACID® (converted to 75 % H_3PO_4) produced compared to product specifications (REMONDIS Aqua Industrie GmbH & Co.KG. 2019)

Elements	Unit	REPACID® specifications	REPACID® from SSA#3		
			Charge 1	Charge 2	Charge 3
H_3PO_4	%	75	75	75	75
H_2SO_4 (S_{Total})		0.5-1	0.80	0.89	0.96
Al		0.1-1	<0.02	<0.02	<0.02
Fe		0.1-1	0.17	0.25	0.41
Ca		<0.05	<0.02	<0.02	<0.01
Mg		<0.05	<0.002	<0.002	<0.01
Cd	ppm	<1	<0.22	<0.21	<0.1
Cu		<3.5	<2.2	<2.2	<1
Ni		<3	<2.2	<2.2	<1
Pb		<3	<2.2	<2.2	<1

The quality of this phosphoric acid (trademark: REPACID®) can be compared with commercial purified phosphoric acid (technical grade). Moreover, this process enables various different levels of purity to be generated for different applications.

Gypsum

The produced synthetic gypsum has low water content and therefore high transportability. The measured metal content lies below the limitations for plasterboard recycling plants, so there is no danger to people or the environment. Tests from a company specialised in the production and distribution of high quality and individual calcium sulfate showed that the recrystallisation from the present dihydrate form to calcium sulfate semi-hydrate is possible, which makes it fundamentally suitable as a raw material for the production of building materials. As such, the by-product should have no coloring (Figure 3.1.9), which can be an additional quality criterion.

Figure 3.1.9: Synthetic gypsum produced by TetraPhos® process (crystallisation/separation step) (Picture: REMONDIS Aqua Industrie GmbH & Co.KG./P. Herr)

Synthetic Gypsum from this process, as well as the gypsum currently processed from flue-gas cleaning of power plants, can be used in the construction industry.

Metal salt

The metal salts can be directly used as precipitation agents in the wastewater treatment plant.

External investigations done by the Westfälisches Umwelt Zentrum Höxter (2020) confirmed the basic effectiveness of the precipitant produced. Test series (Figure 3.1.10) were carried out in comparison with the precipitant normally used at the Bottrop wastewater treatment plant (here: Green salt Fe(II)SO_4). In the first sequence of investigation, treated wastewater was mixed with potassium phosphate (for achieving a significant P-concentration of 150 mg/L for the investigations of the sludge precipitated), in a second sequence activated sludge from the Bottrop wastewater treatment plant was used, which was also increased with potassium phosphate to an initial concentration of approx. 5 mg/L (corresponds to real conditions). The precipitants were added in different dosages (molar ratio: 1, 2 and 3 mol Metal-Ion/mol P).

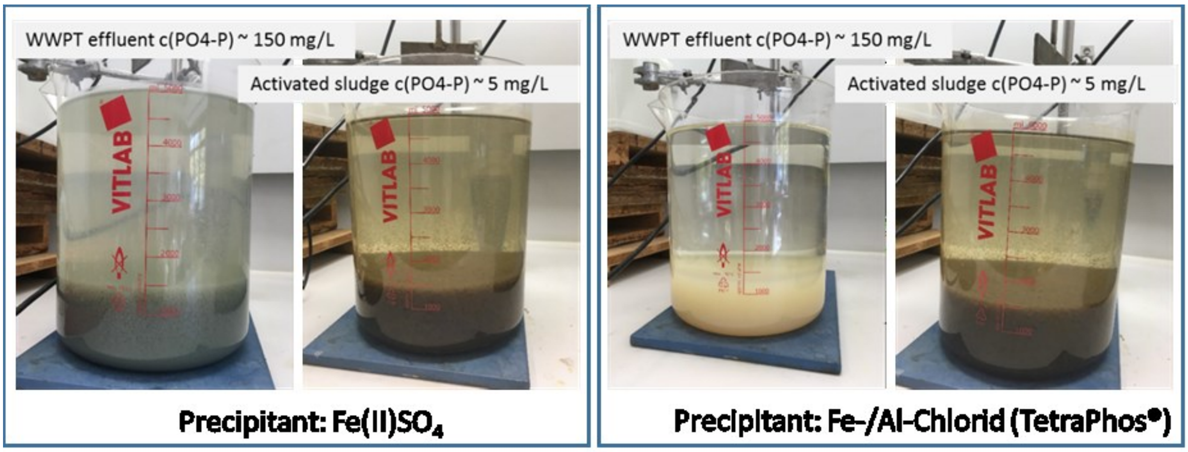


Figure 3.1.10: Exemplary pictures taken during the experiment (here after contact time in the settling phase of the sludge) (Picture: Westfälisches Umwelt Zentrum/V. Pick)

In addition to the general effectiveness, positive tendencies were also observed in comparison with green salt:

- The supernatant after the sedimentation process was clearer;
- The dewatering characteristics seemed to show better results.

However, due to the acidic nature of the metal salt solution, it is necessary to adjust the pH to maintain the buffer capacity. In order to confirm the results, technical scale experiments should be carried out at the location.

SSA residues

The washed SSA residue contains >50 % dry matter, is semi-solid, and is landfilled or recycled. The phosphorus-depleted residue weighs approximately the same as the original SSA, which means no extra disposal costs, if any. This material can also be an additive for different construction processes, so the amount of waste can be reduced further (Figure 3.1.11).

Figure 3.1.11: SSA residues produced by TetraPhos® process (Picture: REMONDIS Aqua Industrie GmbH & Co.KG./P. Herr)

Some inorganic pollutants are leached from the SSA residue during the TetraPhos® process, so the landfill class decreases compared to the SSA. The demarcation from landfill class III to landfill class II raises the chance to decrease the disposal costs. However, recycling is preferable and is the subject of ongoing investigations by REMONDIS.

Conclusion on the pre-industrial demonstration

A summary of key results (REMONDIS Aqua Industrie GmbH & Co.KG. 2019) regarding quality is given:

- Phosphorus elution rate of >85 % was achieved with SSA from the Bottrop SSIP without coal conditioning and from the Lünen incinerator.
- In all phases of the investigation, a product with consistently high quality was achieved.
- The produced by-products – gypsum and metal salts – are of high quality with low levels of contaminants, which makes recovery possible.
- The SSA residue from Bottrop shows a better landfill class than the raw SSA, which could reduce disposal costs. The residue from Lünen showed no change in landfill class.

In this respect, this new multi-stage process not only recovers phosphate as phosphoric acid but also calcium as gypsum and aluminium and iron as a metal salt solution.

3.1.3.2 *Phos4Life™ process*

Proof of Concept (POC) tests (Técnicas Reunidas 2020) have been performed with Phos4Life™ technology on SSAs of the Emscher-Lippe region. The scope of the laboratory test work has covered the following tasks:

- Physical and chemical characterisation of SSAs representative samples;
- Preliminary Leaching tests devoted to solubilize phosphorus from each of the samples;
- Preliminary Impurities Removal tests to evaluate elimination of detrimental elements for the technology;
- Preliminary H_3PO_4 Solvent extraction tests to determine phosphoric acid recovery and purification.

As previously described, mixtures of different SSAs were used in further investigations in addition to the comparative SSA from Bottrop (SSA#3, Table 3.1.5 and Table 3.1.4).

- SSA#3: SSA from Bottrop
- SSA#4: Blend of SSAs with high industrial influence
- SSA#5: Blend of SSAs with less industrial influence

3.1.3.2.1 Process description

Figure 3.1.12 illustrates the different stages of the Phos4Life™ process. In the first step, sulfuric acid is added to the SSAs. Phosphorus and accompanying substances are dissolved. The formed gypsum remains in the SSA residue and is removed from the process and can be used in the building materials industry. The core process involves purifying the raw phosphoric acid by solvent extraction. Optionally, iron can be separated in advance (also by solvent extraction). Iron chloride and phosphoric acid are brought to a commercial concentration by evaporation of water. Heavy metals can be removed separately from the process and recycled.

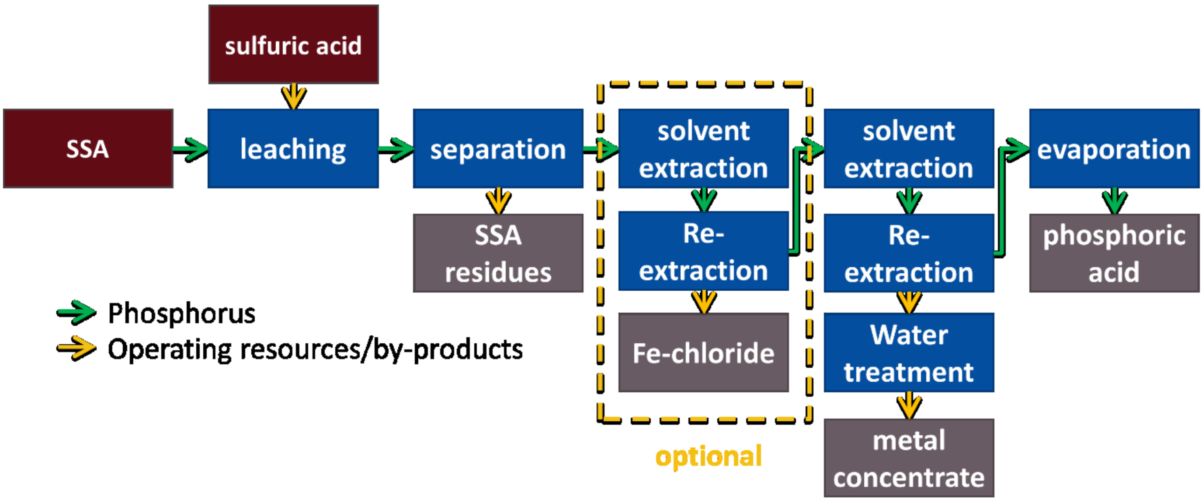


Figure 3.1.12: Process scheme of Phos4Life™

3.1.3.2.2 Proof of concept tests

Preliminary leaching tests

Tested variables:

Sulfuric acid dose:	0.7 – 3.7x (2.5x) times stoichiometric dose
Pulp density:	400 (200) g/L
Reaction time:	20 – 120 minutes
Temperature:	40 – 80 °C

Figure 3.1.13: Experimental set up for leaching stage for the Phos4Life™ process (Picture: Técnicas Reunidas)

Results under selected conditions for leaching confirming test:

- SSA#3 - Leaching efficiencies: P = 86-97 %, Fe = 3-30 %, Al = 29-49 %
- SSA#4 - Leaching efficiencies: P = 93-94 %, Fe = 12-18 %, Al = 42-45 %
- SSA#5 - Leaching efficiencies: P= 95-96 %, Fe = 11-36 %, Al = 42-49 %

Preliminary impurities removal tests

<u>Tested variables:</u>

Organic to Aqueous volumetric ratio (O/A):	0.5 to 8
Contact Time:	10 minutes
Temperature:	25 °C

Figure 3.1.14: Experimental set up for Solvent extraction stage (Fe-extraction) (Picture: Técnicas Reunidas)

Preliminary results:

- SSA#3: Reduction of Fe content from 20.2 g/L in PLS → 9.5 g/L
- SSA#4: Reduction of Fe content from 3.7 g/L in PLS → 3.1 g/L
- SSA#5: Reduction of Fe content from 21.5 g/L in PLS → 18.2 g/L

In case of low Fe-concentration in the liquor, extraction is not worthy.

As illustrated in Figure 3.1.12 this unit is optional and depends on: [i] iron partition in previous leaching stage, and [ii] local residue governance laws.

Preliminary H_3PO_4 solvent extraction tests

<u>Tested variables:</u>

Organic to Aqueous volumetric ratio (O/A):	0.5 to 8
Contact Time:	10 minutes
Temperature:	25 °C

Figure 3.1.15: Experimental set up for Solvent extraction stage (H_3PO_4-extraction) (Picture: Técnicas Reunidas)

Preliminary results:

- SSA#3: H_3PO_4 extraction yields are very positive; these results are in accordance with other Phos4Life^{TM} applications;

- SSA#4: low phosphoric concentration in the feeding solutions; extraction is not as effective as for other Phos4Life^{TM} applications;
- SSA#5: H_3PO_4 extraction yields are very positive these results are in accordance with other Phos4Life^{TM} applications.

Conclusion of the POC tests

Preliminary results from POC-Tests clearly suggest that Phos4Life™ technology is suitable to purify phosphoric acids from SSA#3 and #5.

Phosphorus leaching rate was >80 % in all cases, meeting legal requirements. The iron fraction was up to 30 % (SSA#3), but depending on the elution parameters it can be pushed to a very low level. The aluminium elution into the liquid phase is in the range of 30 to 50 %.

For SSA#4 it is mandatory to proceed with further experimentation. Jelling of the filtered liquor from leaching tests makes this sample not suitable for standard process conditions.

3.1.3.3 *PARFORCE process*

In the lab-tests and in the pilot demonstration, all the main process steps shown in the process diagrams below (Figure 3.1.16 and Figure 3.1.20) were tested. The project also includes the determination of material flows, of chemical and energy consumption as well as the qualified estimation of investment and operating costs for the recovery of phosphoric acid with the PARFORCE process from three SSA samples provided by the Lippeverband.

Analogous to the "Phos4Life™" POC tests (3.1.3.2), three different samples, SSA#3 (SSA Bottrop without coal conditioning), SSA#4 (SSA blend with high industrial influence) and SSA#5 (SSA blend with low industrial influence), were used (Table 3.1.5 and Table 3.1.4).

3.1.3.3.1 Lab-tests

Process description for lab-tests

Figure 3.1.16 illustrates the different stages of the PARFORCE process during the lab-tests. In the first step, diluted hydrochloric acid is added to the SSA to elute the phosphorus (approx. 15 % HCl). Analogous to the other processes described, the SSA residue is then separated and the eluate (crude phosphoric acid) is further processed.

Following the wet solid separation, the iron fraction is first separated from the eluate by solvent extraction. In this process, portions of the dissolved phosphorus are also transferred to the extractant. To minimize P losses, the co-extracted P fraction is selectively separated in a first re-extraction step and returned to the process. In the second re-extraction step, the iron fraction is selectively separated and discharged as iron sulfate (by-product).

This is followed by further purification of the crude phosphoric acid by electrodialysis. In this process, one and two valent ions such as calcium and magnesium as well as most toxic heavy metal ions are selectively separated from the crude phosphoric acid. The separated concentrate stream is neutralized and precipitated by-products, including phosphorus, are returned to the process. After neutralization, a Ca-/Na-chloride solution is produced, which can be used directly as a brine or, after evaporation as a road salt, or as a de-icing agent in winter.

The diluate stream (phosphoric acid) is brought to marketable concentrations by evaporation. The resulting phosphoric acid basically meets the quality requirements of the fertiliser industry. Further processing steps can be integrated to produce a higher-grade (technical grade acid) product.

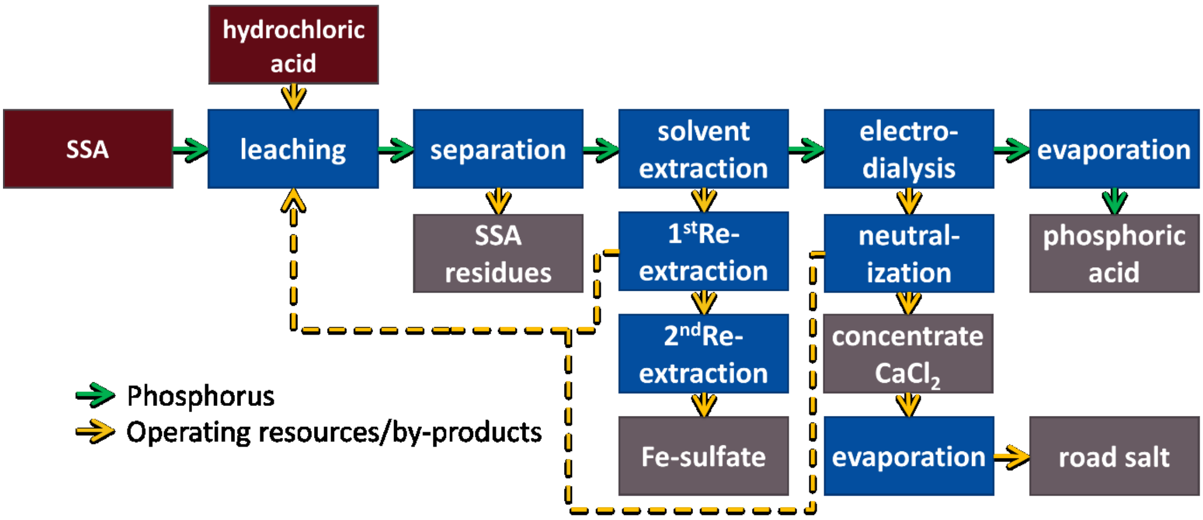


Figure 3.1.16: Process scheme of PARFORCE technology used in the lab-tests

Leaching rates

The leaching rates of the relevant main components (P, Fe, Ca and Al) determined are as follows (Table 3.1.7).

Table 3.1.7: Leaching rates for main compounds of different samples, achieved with the PARFORCE process (PARFORCE Engineering & Consulting GmbH 2020)

Sample	Al	Ca	Fe	P
	(%)			
SSA#3	36.3	94.2	7.8	94.2
SSA#4	58.9	79.1	15.7	92.5
SSA#5	56.3	90.6	10.7	93.8

The result of the leaching tests showed very high leaching rates of over 92 % for phosphorus and over 90 % for calcium, indicating a high proportion of calcium phosphate species in the material and mineral phases of the SSA, which is advantageous for recovery. Values for iron and aluminium are in the usual range, with leaching rates for iron ranging from 8 % (SSA#3) to 16 % (SSA#4). In addition, the SSA has relatively large grain sizes, which facilitates the filtration of the digestion solution.

Phosphorus balance

From the results of the lab investigation, a phosphorus balance was created on the recovery of P from the used SSA (average) with the PARFORCE process, the results of which are displayed in Figure 3.1.17. For each of the process steps: elution, solvent extraction, and electrodialysis, independent balances were created and then linked to show the whole process. The evaporator step was not considered in the balance, because no phosphorus exits the system here.

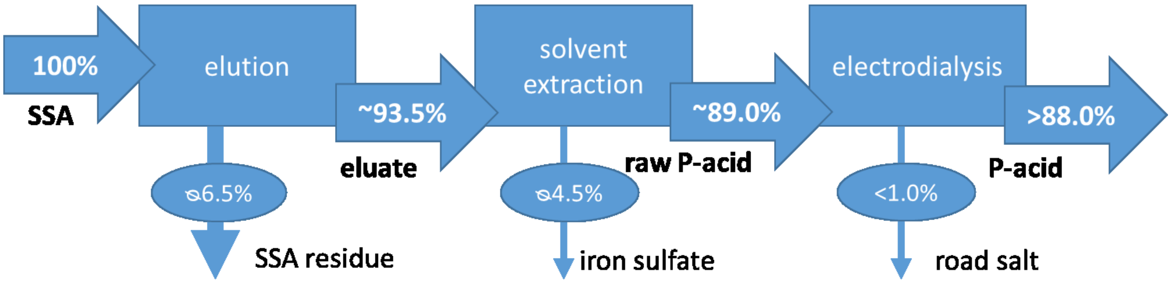


Figure 3.1.17: Phosphorus balance obtained with the PARFORCE process applied to SSA of Bottrop WWTP without coal conditioning as well as blends with high and low industrial influence (see chapter above) (own illustration following (PARFORCE Engineering & Consulting GmbH 2020)

The presented balance shows that the efficiency of the process in terms of phosphate mobilisation is very high (approx. 93.5 %). From the eluate (raw phosphoric acid to the marketable product), only about 4.5 % of the phosphorus is incorporated into metal salt (precipitant) and a small part is removed from the system during the processing of road salt.

Product quality

Phosphoric acid

Figure 3.1.18 shows the phosphoric acids as slightly yellow-greenish, highly viscous solutions after evaporation. Only the phosphoric acid from SSA#4 is very viscous or gel-like. The concentrations of the phosphoric acids produced after evaporation range from 26 to 56 wt % H_3PO_4 and are thus still relatively low.

In the case of SSA#4 and #5 in particular, this is due to the fact that evaporation was stopped because of the viscosity achieved, owing to the fact that aluminium extraction was not carried out after electrodialysis as a further purification step. Contained aluminium is presumably responsible for gel formation, which explains the higher viscosity. However, the aluminium extraction could be implemented - as far as necessary for commercialisation. The decisive factor here is the final SSA composition with the Al leaching rates during digestion.

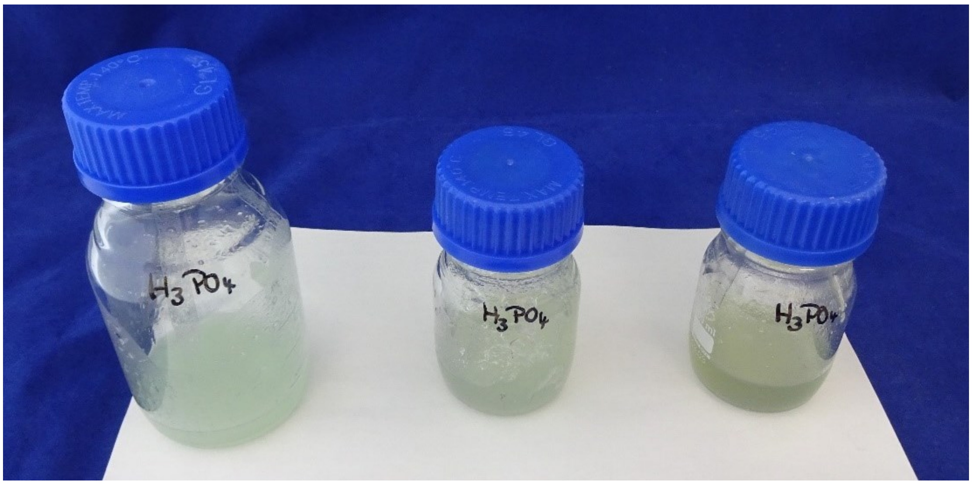


Figure 3.1.18: Phosphoric acid samples after evaporation (SSA#3 to #5 from left to right) (PARFORCE Engineering & Consulting GmbH 2020)

In the case of SSA#3, a concentration was achieved which can basically be used directly for fertiliser production at low transport distances (up to approx. 200 km). Gel formation is much less pronounced in SSA#3, so that even higher concentrations can be achieved here.

Table 3.1.8 shows that all the heavy metals considered were depleted many times over in the P acid compared to the starting material. The elements Cd, Cu, Hg and Pb are below the detection limit in all processed SSA.

Table 3.1.8: Overview of the ingredients of the produced phosphoric acid samples converted to 75 % H_3PO_4 (PARFORCE Engineering & Consulting GmbH 2020)

Elements	Unit	SSA#3	SSA#4	SSA#5
H_3PO_4 (measured)	%	56.3	26.2	46.5
purity		93.3	92.6	92.5
H_3PO_4 (calculated)		75	75	75
Al		3.5	5.1	5.2
Ca		0.57	0.23	0.18
Fe		0.02	0.22	0.16
K		0.01	<0.01	<0.01
Mg		0.28	0.11	0.15
Na		0.71	0.23	0.19
S		0.23	0.09	0.21
As	ppm	29	20	20
Cd		<0.3*	<0.3*	<0.3*
Cr		24	52	27
Cu		<1*	<1*	<1*
Hg		<0.1*	<0.1*	<0.1*
Mn		243	102	115
Ni		4	5	2
Pb		<3*	<3*	<3*
Zn		2	12	2

* Measured values in the original sample are below the limit of quantification.

For the fertiliser-relevant element Cd, all samples are below the detection limit. The limit value of the Fertiliser Ordinance (Germany) for cadmium of 50 ppm (reference basis P_2O_5 content) is thus clearly undercut.

The main impurity in phosphoric acid is aluminium. Aluminium is *a priori* not a problem when P acid is used in the fertiliser industry. With regard to the purity of the phosphoric acid, the results are between 92.6 % and 93.3 %, a higher purity can be achieved by optimising the electrodialysis, since Ca, Mg and Na in particular can be further separated. A purity up to 95 % is thus possible even without additional aluminium extraction.

The results obtained during the acid evaporation trials and the analysis of the concentrated phosphoric acid show that, at least in the case of SSA#4 and SSA#5, aluminium separation prior to evaporation on an industrial scale is recommended. The separation of aluminium on the one hand avoids the gel-like consistency and on the other hand increases the phosphoric acid purity.

Metal salt

In the solvent extraction step, >99 % of the iron contained is removed in the form of iron(II)sulfate. The contained phosphate impurities (Table 3.1.9) could still be removed by a downstream precipitation. With the high P-leaching rates of over 92 % and the recycling of more than 70 % of the co-extracted phosphate, this is not necessary to meet the German sewage sludge ordinance. However, it must be examined to what extent the iron solution can be used directly as precipitation salt (green salt) again in the sewage treatment plant. In addition to the high levels of phosphorus, the copper and lead contents are also critical for direct use.

Table 3.1.9: Overview of the ingredients of the produced metal salt (PARFORCE Engineering & Consulting GmbH 2020)

Sample	Al	Ca	Fe	P	Cu	Pb	Zn	Cd	Cr	Ni
	(mg/L)									
SSA#3	210	632	7,789	3,095	175	25	<5	<5	<5	<5
SSA#4	363	632	9,069	1,978	279	55	<5	<5	<5	<5
SSA#5	225	484	7,817	2,540	241	36	<5	<5	<5	<5

Road salt

The road salt (Figure 3.1.19) produced can be classified according to DIN EN 16811-2 as a road salt mixture with a calcium chloride content of at least 10 % by weight with regard to the total amount of chloride salts.

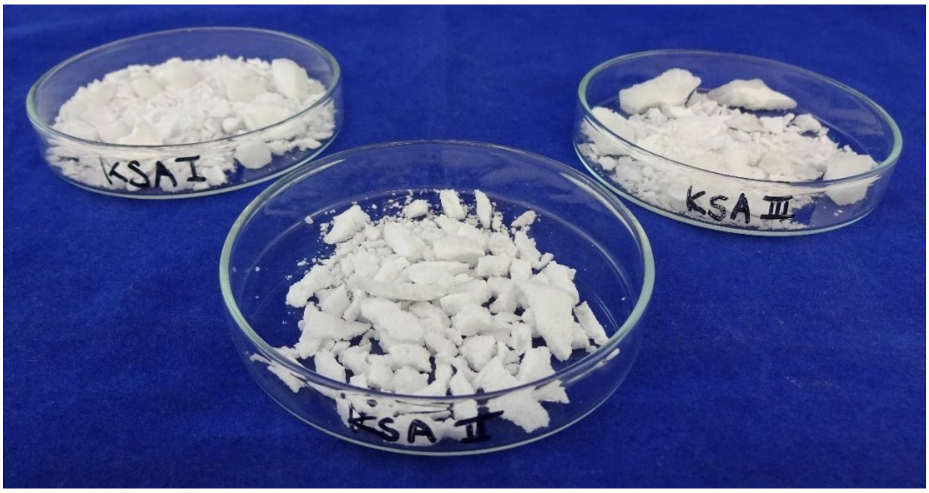


Figure 3.1.19: Road salt samples after drying (SSA/Sample#1 to #3 from left to right) (PARFORCE Engineering & Consulting GmbH 2020)

The results of the analyses listed in Table 3.1.10 show that the road salt produced out of the three SSA samples is in conformity with the standard with regard to the presented parameters in comparison with the limit values of DIN EN 16811-2.

Table 3.1.10: Overview of the ingredients of the produced road salt in comparison with the limit values on DIN EN 16811-2 (PARFORCE Engineering & Consulting GmbH 2020)

	$CaCl_2$	SO_4^{2-}	Al	As	Pb	Cd	Cr	Cu	Ni	Hg	Zn
	(%)		(mg/kg)								
*Limit value**	*>10*	*<1.5*	*<50*	*<2.5*	*<5*	*<2*	*<5*	*<5*	*<5*	*<0.5*	*<20*
SSA#3	93	0.44	31	<0.8	<2	<0.2	1	3	3	<0.1	9
SSA#4	82	0.42	41	<0.8	<2	<0.2	<1	<1	<1	<0.1	3
SSA#5	87	0.48	48	<0.8	<2	1.4	1	2	3	<0.1	5

*DIN EN 16811-2

Conclusion on the lab-tests

All the process steps listed (Figure 3.1.16) were carried out on a laboratory scale and samples were prepared for the main product, phosphoric acid, and the by-products, including road salt. Each process step includes measurements that were used to verify the PARFORCE calculation model. The obtained results form the basis for the calibration of the PARFORCE calculation model to determine the material flows and for the design of the process steps for P recovery using the PARFORCE technology.

The three SSA samples investigated have relatively low P contents. The investigations have shown that the phosphorus content is not the sole criterion for evaluating the technical effort for phosphorus recovery. Among other things, the calcium content is also of decisive importance. A higher Ca content leads to higher acid consumption and energy requirements as well as to higher necessary capacities in the plant components.

The lab-tests results shown that the technology achieves a sufficiently high recovery rate (>88 %) for all three SSA samples used. The depletion of pollutants (heavy metals) was satisfactorily demonstrated. For the production of concentrated P-acid, an additional elimination of aluminium is recommended, which presumably prevents the occurrence of gel formation. The road salt produced as a by-product is of high quality and marketable. The metal salt solution (iron(II)sulfate) presumably has to undergo further treatment steps for direct use as a precipitant.

3.1.3.3.2 Pilot demonstration

Process description for pilot-trials

Figure 3.1.20 illustrates the different stages of the PARFORCE process during the pilot-demonstration. The basic principle has already been explained in section above (0). In contrast to the process set-up for the lab-tests, an ion exchanger (1st IO-Exchange) was used instead of solvent extraction in the pilot tests for Fe/Al separation. In addition, an optional ion exchange step (2nd IO-Exchange) was used to reduce the previous described problems of gel formation by extended aluminium separation.

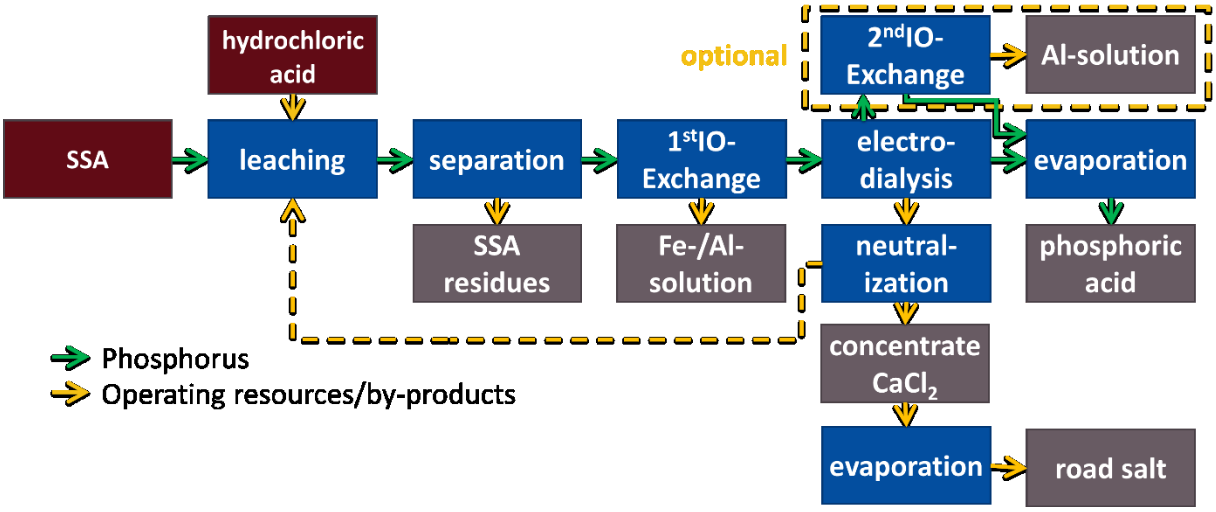


Figure 3.1.20: Process scheme of the PARFORCE technology during pilot demonstration

Leaching rates

The leaching rates in the pilot tests are increased compared to the results from the laboratory tests, especially for iron (Table 3.1.11). The separation of the liquid phase was carried out with a chamber filter press. Due to the extended filtration time in this aggregate, the targeted elution time was considerably exceeded, resulting in increased dissolution of the constituent substances such as iron, aluminium and calcium. The phosphorus extraction rate of 93.9 % is absolutely comparable to the leaching rate in the laboratory tests.

Table 3.1.11: Leaching rates for main compounds of used samples SSA#5 compared to the results from the lab-tests, achieved with the PARFORCE process (PARFORCE Engineering & Consulting GmbH 2020, 2021)

Sample	Al	Ca	Fe	P
	(%)			
SSA#5 (lab)	56.3	90.6	10.7	93.8
SSA#5 (pilot)	68.2	94.2	31.4	93.9

Phosphorus balance

From the results of the pilot investigation, a phosphorus balance was created over the recovery out of the used sample (SSA#5) through the PARFORCE process, the results of which are displayed in Figure 3.1.21. For each of the process steps: elution, ion exchange (1st and 2nd IO-Exchange), and electrodialysis, independent balances were created and then linked to show the whole process. The evaporator step was not considered in the balance, because no phosphorus exits the system here.

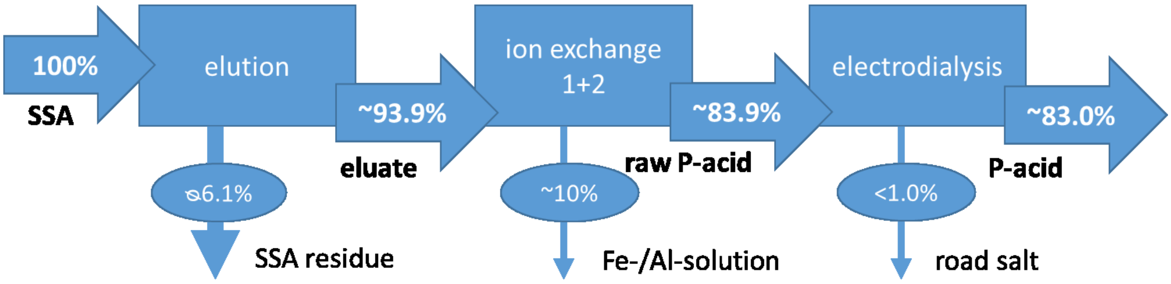


Figure 3.1.21: Phosphorus balance obtained in the pilot-tests with the PARFORCE process applied to sample SSA#5 (own illustration following PARFORCE Engineering & Consulting GmbH (2021))

The presented balance shows that the efficiency of the process in terms of phosphate mobilisation is very high (approx. 93.9 %). However, in contrast to the lab-tests, the loss of phosphorus in iron and aluminium separation by ion exchange is relatively high (approx. 10 %). According to PARFORCE, there is still potential for optimisation in the operation of the exchangers. Analogous to the lab-tests, the P discharge via the road salt is very low.

Product quality

Phosphoric acid

Figure 3.1.22 shows the phosphoric acids produced in the pilot-tests. The left picture shows phosphoric acid produced without additional aluminium separation (2nd ion exchanger). Just like the acid produced in the lab-tests (Figure 3.1.18), it has a slightly yellow-greenish color. The concentration after evaporation is 70 wt % H_3PO_4 and thus far exceeds the result from the lab-tests with 46.5 wt % H_3PO_4 (Table 3.2.2). The gel formation that occurred in the laboratory tests was not observed to this extent.

The picture on the right (Figure 3.1.22) shows the phosphoric acid produced after additional aluminium separation (2nd ion exchanger). The concentration after evaporation is 66 % (Table 3.2.2). The dark coloration is striking. According to PARFORCE, the reason for this is the discoloration property of the very dark ion exchange resin used. A prior conditioning of the resin can avoid the coloration of the produced phosphoric acid.

Figure 3.1.22: Phosphoric acid samples after evaporation (left: without Al-separation, right: after Al-separation) (PARFORCE Engineering & Consulting GmbH 2021)

Table 3.1.12 shows the composition (normalized to a concentration of 75 wt % H_3PO_4) of the two phosphoric acids generated in the pilot tests (right columns) in comparison with the phosphoric acid from the lab-tests with Sample SSA#5 (left column). The phosphoric acid generated without optional ion exchangers (just 1st IO-Exchange) for additional aluminium removal has a lower purity of 88.1 % than phosphoric acid from the lab-tests. The aluminium and arsenic contents are indeed lower. But all other accompanying substances show higher concentrations in direct comparison.

The phosphoric acid after additional purification by the optional ion exchanger (2nd IO Exchange) has a high purity of 99.1 %. Almost all accompanying substances could be significantly reduced by the use of the 2nd ion exchanger stage.

Table 3.1.12: Overview of the ingredients of the produced phosphoric acid samples of used SSA samples#5 compared to the results from the lab-tests converted to 75 wt % H_3PO_4 (PARFORCE Engineering & Consulting GmbH 2020, 2021)

Elements	Unit	SSA#5 (lab-tests, Solvent Extraction)	SSA#5 (pilot tests, 1st IO-Exchange)	SSA#5 (pilot tests, 2nd IO-Exchange)
H_3PO_4 (measured)	%	46.5	70.0	66.0
purity		92.5	88.1	99.2
H_3PO_4 (calculated)		75		
Al		5.2	4.6	0.3
Ca		0.18	0.6	0.01
Fe		0.16	0.6	0.1
K		<0.01	0.02	<0.01
Mg		0.15	0.4	0.02
Na		0.19	1.4	0.1
S		0.21	N/A	N/A
As	ppm	20	<5*	<5*
Cd		<0.3*	<5*	<5*
Cr		27	66.4	29.6
Cu		<1*	116.8	<5*
Hg		<0.1*	<5*	<5*
Mn		115	395.4	22.7
Ni		2	11.8	<5*
Pb		<3*	18.2	<5*
Zn		2	56.8	<5*

* Measured values in the original sample are below the limit of quantification.

For the fertiliser-relevant element Cd, all samples are below the detection limit. The limit value of the Fertiliser Ordinance (Germany) for cadmium is of 50 ppm (reference basis P_2O_5 content) is thus clearly undercut. The main impurity in phosphoric acid is aluminium. With regard to the purity of the phosphoric acid, the results are up to 99.2 %, a higher purity can be achieved by optimising additional aluminium extraction.

The results obtained during the acid evaporation in the lab-tests (0) and the analysis of the concentrated phosphoric acid (Table 3.1.12) show that aluminium separation is recommended. The separation of aluminium on the one hand avoids the gel-like consistency and on the other hand increases the phosphoric acid purity.

Metal salt

The 1st IO-Exchanger already removes a large proportion of the iron (93 %) and 35 % of the aluminium from the crude phosphoric acid. With the use of the 2nd IO-Exchanger, the retention rate for both metals increases to >99 %.

In order to investigate different options for the generation of Fe- and Al-based solutions, the two ion exchangers used were washed with different regeneration agents (see Table 3.1.13). This allows chloride- or sulfate-based precipitants to be generated as required. Table 3.1.13 shows the composition of the Fe/Al solutions.

Table 3.1.13: Overview of the ingredients of the produced metal salt solutions (PARFORCE Engineering & Consulting GmbH 2021)

IO-Ex	Reg. agent	Al	Ca	Fe	P	Mg	Na	K
(-)	(-)	(mg/L)						
1st	HCl (15 %)	1,186	<20	3,245	2,802	<20	-	-
1st	$Na_2S_2O_3$ (1M)	1,006	1,750	4,748	2,959	308	-	-
2nd	HCl (15 %)	5,704	114	511	1,604	521	857	4
2nd	H_2SO_4 (25 %)	5,488	112	430	1,830	446	897	4

It must be examined to what extent the Fe-/Al-solutions can be used directly as precipitation salt again in the sewage treatment plant. It is mentioned that the high levels of phosphorus are critical for direct use. The contained phosphate impurities could still be removed by a downstream precipitation. With the high P-leaching rates of over 92 % and the recycling of 65 % of the co-extracted phosphate, this is not necessary to comply with the German sewage sludge ordinance.

Road salt

In addition to road salt, a usable road salt brine was also produced in the pilot tests. The road salt and the brine are shown below in Figure 3.1.23. On the one hand, the production and supply as a brine has advantages due to the lower operating costs – additional process steps for the production of a dry road salt are not necessary. On the other hand, this requires higher storage capacities as well as application possibilities in the neighbourhood of the production site.

Figure 3.1.23: Road salt samples after drying (left) and brine (right) (PARFORCE Engineering & Consulting GmbH 2021)

The results of the analyses listed in Table 3.1.14 show that the road salt produced in the pilot out of sample SSA#5 is in conformity with the standard with regard to the parameters shown in comparison with the limit values of DIN EN 16811-2.

Table 3.1.14: Overview of the ingredients of the produced road salt compared to the results from the lab-tests and the limit values on DIN EN 16811-2 (PARFORCE Engineering & Consulting GmbH 2020, 2021)

	$CaCl_2$	SO_4^{2-}	Al	As	Pb	Cd	Cr	Cu	Ni	Hg	Zn
	(%)		(mg/kg)								
Limit value*	*>10*	*<1.5*	*<50*	*<2.5*	*<5*	*<2*	*<5*	*<5*	*<5*	*<0.5*	*<20*
SSA#5 (lab)	87	0.48	48	<0.8	<2	1.4	1	2	3	<0.1	5
SSA#5 (pilot)	91	0.63	10	<1	<1	<1	1	<1	2	<1	8

In direct comparison with the road salt produced in the lab-tests, it can be seen that many of the constituents listed in Table 3.1.14 are present in lower concentrations due to the modified process control with the use of ion exchangers. The quality of the product produced was therefore increased.

The conformity of the brine is based on the contents of the dry salt, therefore the compliance with the limits for the brine is also given. The solid-free brine has a $CaCl_2$ content of approx. 27.5 % by weight and is suitable for use in winter road maintenance.

Conclusion on pilot demonstration

All the process steps listed (Figure 3.1.20) were carried out on a pilot scale and samples were prepared for the main product, phosphoric acid, and the by-products, including brine and road salt. Each process step includes measurements that were used to verify the PARFORCE calculation model. The obtained results form the basis for the calibration of the PARFORCE calculation model to determine the material flows and for the design of the process steps for P recovery using the PARFORCE technology.

The pilot tests have largely confirmed the results of the lab-tests. Even if the phosphorus recovery rate is lower at >83 %. The use of ion exchange resins as a replacement process for solvent extraction has positive effects on the quality of the products. The additional elimination of aluminium has greatly reduced the gel formation that occurred in the lab-tests during the production of concentrated acid. Furthermore, the additional cleaning step significantly improved the removal of accompanying substances and pollutants (heavy metals).

The quality of the road salt and/or brine produced as a by-product was increased. It was shown that the generation of the metal salt solution can be carried out as required by using different regeneration agents for washing the ion exchange. However, in the Fe/Al solutions generated from the 1st IO-Exchanger, the co-extraction of phosphorus is higher in direct comparison with the lab-tests. According to PARFORCE, there is still some potential for optimisation in the regeneration step of the ion exchange. On the basis of the present results, the direct use of the Fe/Al solutions as precipitant is probably not possible without further treatment steps.

In conclusion, the pilot tests have shown that despite increased leaching rates of the accompanying substances, a phosphoric acid with very low impurities could be produced.

3.1.3.3.3 LCA for PARFORCE

The PARFORCE-process has been included in the LCA-LCC works done within Phos4You (cf. chapter 5).

3.1.4 Discussion of results for I2 operation

The quality and purity of the phosphoric acid produced is quite variable, depending on the effectiveness of the purification processes applied, and carries small amounts of accompanying substances in accordance with the starting substance (SSA). However, it can be stated that the phosphoric acids produced in the "Phos4You" project are of marketable quality.

However, the investigations carried out only provide a snapshot, since the composition of the SSAs used will change (seasonally) during the ongoing process. The resilience of the processes/procedures in continuous operation will only become apparent when they are implemented industrially over a longer period of time.

Particularly with regard to the quality and possible uses of the by-products and residual materials generated with wet-chemical P-recovery processes, there are still some uncertainties. Open questions about disposal routes or stable sales markets or recycling possibilities exist, but still need to be validated.

In the context of advancing technological implementation, the following points will play an essential role in the efficient design of phosphorus recovery from SSAs by "wet-chemical" processes:

- Process optimisation/adaptations also in terms of operating chemical (including mineral acid - eluate) and energy requirement
- Process design in terms of by-product generation and quality

3.1.5 Conclusion for I2

In conclusion, it can be stated that the technological solution of "wet-chemical" phosphorus recovery from SSAs is generally applicable and that the legal requirements, such as those of the German Sewage Sludge Ordinance (target: recovery rate > 80 %), can be met.

Further technological implementation will demonstrate feasibility and answer any remaining questions. The processes considered in Phos4You will be implemented on an industrial scale in further projects (Figure 3.1.24). (EUWID 2020; Schneider 2021; Ruhrverband 2021; Schlumberger 2021; AWEL 2018)

- TetraPhos® → Germany, Hamburg 2021
- PARFORCE → Germany, Bottrop 2023
- Phos4Life™ → Switzerland, Zuchwil 2027/2028

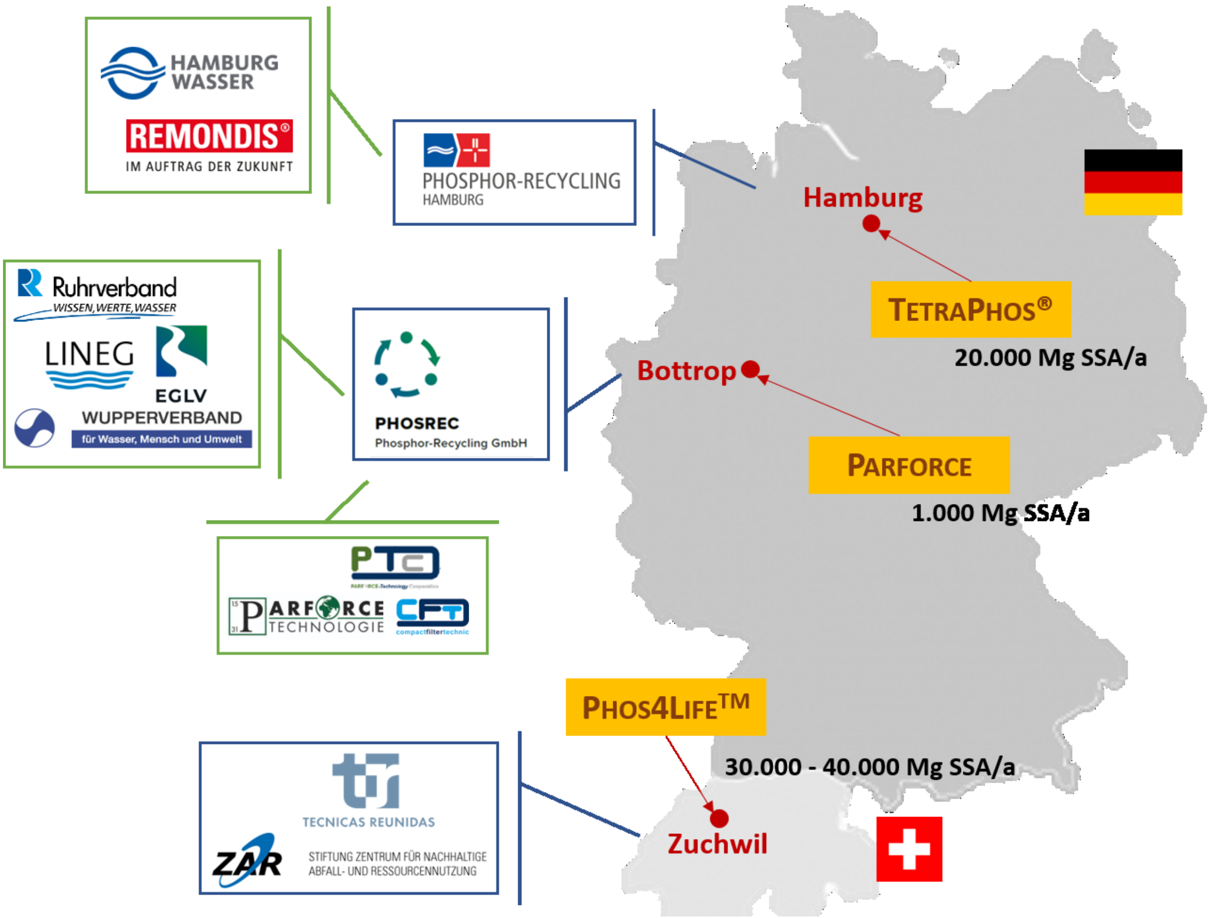


Figure 3.1.24: Outlook on technology implementation of the “wet-chemical” P-recovery processes considered in Phos4You

3.2 Demonstrator I1: Thermochemical solution to recover P from sewage sludge (EuPhoRe®)

Authors: Daniel Klein, Karl-Georg Schmelz, Levent Pamuk, Burkhard Teichgräber (Emschergenossenschaft); Frank Zepke (EuPhoRe GmbH)

Phos4You demonstrated how phosphorus can be recovered from sewage sludge thanks to a thermochemical incineration process. The EuPhoRe® plant built by the Emschergenossenschaft in Dinslaken is the first stand-alone plant of the technology (Klein et al. 2019), i.e. the plant is not combined with e.g. an (existing) power plant.

The EuPhoRe®-process is a 2-stage thermochemical incineration process and consists of a rotary kiln where dewatered sewage sludge is successively dried, reduced and oxidized. In the reduction step (650-750°C), a major part of the volatile matter is already transferred to the gas phase. Besides, the reactivity of the solid phase is increased (Hedvall-Effect), yet leading to a notable transfer of heavy metals to the gas phase. The remainder of the pollutants is subsequently removed during the oxidation step (up to 1.000°C). Additives such as $MgCl_2$ are added to the sludge in order to improve the heavy metals removal through the gas phase. The additives also have a notable influence on the plant availability of the remaining sewage sludge ashes. Given this process, the sewage sludge ash (SSA) of the EuPhoRe®-process is – compared to the SSAs of e.g. a fluidised bed incineration – plant available and has a notably lower heavy metal content (Klose 2018). Figure 3.2.1 illustrates the process.

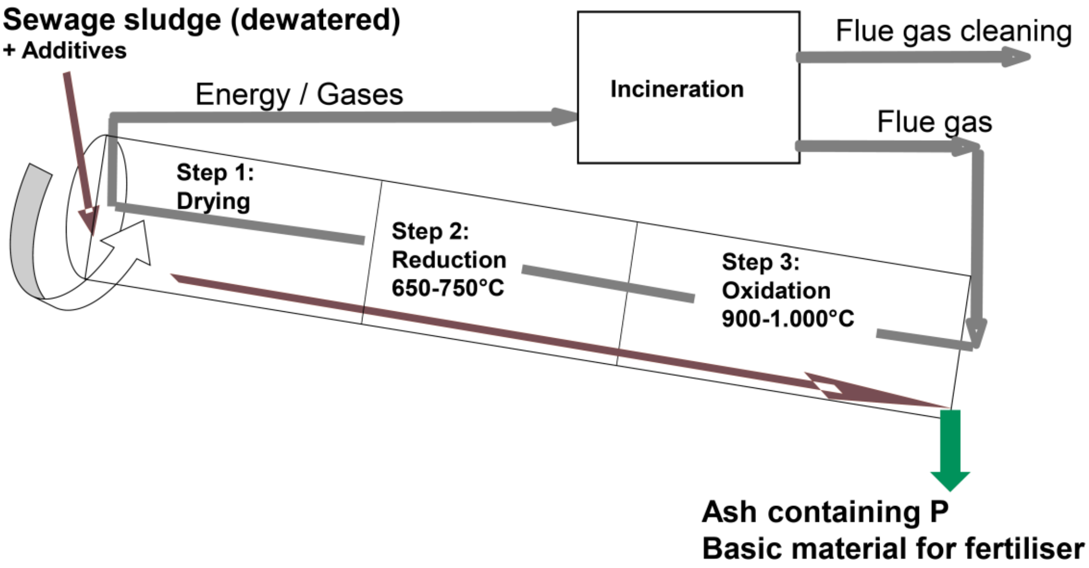


Figure 3.2.1: Schematic overview of the EuPhoRe® process (Klose and Zepke 2010, modified)

3.2.1 Preparation of I1

The decision to assess the EuPhoRe®-technology within a demonstration project based on promising lab-scale results of the EuPhoRe® process (IBU-tec advanced materials AG 2016) carried out with sewages sludges of Emschergenossenschaft (and Lippeverband).

The tests were performed in a lab-scale rotary kiln (capacity: 4 kg of sewage sludge per batch), using pre-dried sludges as input material. As the EuPhoRe® -process, the lab-scale setup consisted of a reduction (pyrolysis) step, followed by an oxidation. To improve heavy metal reduction via the gas phase, $MgCl_2$ was used as additive.

In total, 4 different EGLV-sludges and 3 different additive concentrations (0 %, 3 %, 6 %) were assessed.

With regard to the main goals of the EuPhoRe®-process – reduction of heavy metals and improvement of P-solubility – the results were very promising. Table 3.2.1 gives an overview of the phosphate solubility of the ashes produced, compared to ashes originating from fluidized bad incinerators.

Table 3.2.1: Phosphate solubility of lab-scale trials (IBU-tec advanced materials AG 2016)

Parameter	EuPhoRe®-ashes (range of 4 EGLV ashes)	Other monoincineration-ashes
2% citric acid solubility	65 %-85 %	< 50 %
Ammonium citrate	50 %-80 %	< 40 %

With regard to the heavy metal reduction, the reduction ratio varied in a wide range; depending on the specific element and its base concentration in the input material (sludge). Reduction was generally high for heavy metals such as Pb, Cd, Hg, and Tl. Cu and Zn were also notably reduced. In general, the effect of the additive dosing (3% or 6%) was clearly visible, compared to the trials that were performed without additive (0%).

To conclude, the pilot tests generally showed that the EuPhoRe® process is able to reduce the heavy metal concentrations in the ashes below the relevant limits.

Following additional preparation work and discussions, the EuPhoRe®-demonstrator has been jointly designed in cooperation with the EuPhoRe GmbH and a company specialised in the planning of rotary kilns.

3.2.2 Execution of I1

The construction of the main components of the demonstrator started in 2018; the on-site set-up and assembly started in summer 2018. The construction of the machines was basically finished in late 2018; the implementation of the instrumentation and control engineering was finalised in April 2019.

The sewage sludge input of the demonstrator was maximum 100 kg/h dewatered sludge (DM +/- 25 %); the SSA output obtained ranged 10-15 kg/h.

Hereafter the main features of the different parts of the pilot plant in Dinslaken (including adaptations and optimisations) are described.

Sludge storage

The on-site storage for dewatered sludge had an area of approx. 50 m² and a capacity of 40 t of dewatered sludge. This amount of sludge was sufficient for several weeks of continuous operation, using sludge of the same WWTP and quality. The whole facility was covered (rain- and weather protection) (Figure 3.2.2).

Figure 3.2.2 a and b: Sludge storage (Pictures: Emschergenossenschaft/L. Pamuk)

Sludge hopper

The sludge hopper had a capacity of approx. 10 m³, sufficient e.g. for automatized operation of the plant during week-ends. The whole system was mounted on weighing cells to control sludge input to the rotary kiln (Figure 3.2.3).

Figure 3.2.3 a and b: Sludge hopper and screws (Pictures: Emschergenossenschaft/L. Pamuk)

Sludge transport and feeding

Sludge discharge of the hopper was initially done via a screw system (see above). Since this caused problems in terms of sludge transport, the system was changed over to a drag chain conveyor (Figure 3.2.4). Sludge transport to the input of the rotary kiln was then done *via* a conveyor belt (Figure 3.2.5).

Figure 3.2.4 a and b: Drag chain conveyor (Pictures: Emschergenossenschaft/L. Pamuk)

Figure 3.2.5 a and b: Conveyor belt and rotating cutter (Pictures: Emschergenossenschaft/L. Pamuk)

During the first months of operation, (round) sludge globes were formed on the conveyor belt. Due to the slope of the conveyor belt (24°) and its high velocity, these globes tended to roll back to the lower end of the belt, not reaching the rotary kiln at all. To avoid this, a rotating cutter had been implemented to mechanically destroy the sludge globes on the belt. As an additional optimisation measure, a frequency converter had been implemented to modify the velocity of the belt, if needed.

Dosing of additives and air lock

Shortly before the sludge feeding to the rotary kiln, additives such as $MgCl_2$ were added to the sludge via a small dosing pump. The sludge was then fed into the rotary kiln *via* an air lock system with a double shaft screw, thus avoiding the inflow of ambient air (oxygen) to the kiln (Figure 3.2.6).

Figure 3.2.6 a and b: Dosing of additives and air lock (Pictures: Emschergenossenschaft/L. Pamuk)

Rotary kiln

As described previously, the rotary kiln consisted of three zones. The drying zone was equipped with scoop plates to transport the sludge into the kiln (Figure 3.2.7). In this zone, there was no interior isolation. The scoop system had been repeatedly optimised in order to improve sludge transport through the rotary kiln and to avoid sludge/SSA aggregations, especially with regard to a dryness of approx. 50 % where sludge tended to “stick”.

The reduction- and oxidation zone was equipped with various layers of fireproof stones. The whole construction included “steps” to induce mixing of the material and to avoid that the oxygen in the flue gas was able to oxidize the fixed carbon in the mineral phase. The oxygen was not able to diffuse into the SSA bed (Figure 3.2.7).

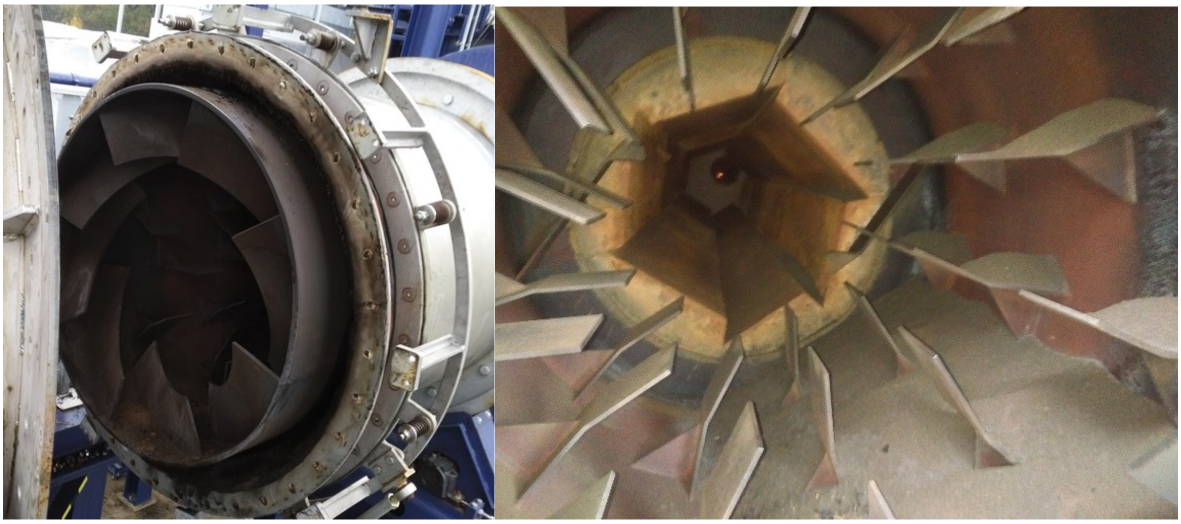


Figure 3.2.7 a and b: Inside views of the rotary kiln (Pictures: Emschergenossenschaft/L. Pamuk)

Given scoop, tilt and rotation, the sewage sludge/the SSA was transported to the end of the rotary kiln (i.e., the oxidation zone) by gravity. Total retention time was approx. 4-6 hours.

During the first periods of operation, the whole rotary kiln had been externally isolated as well to reduce energy losses due to radiation.

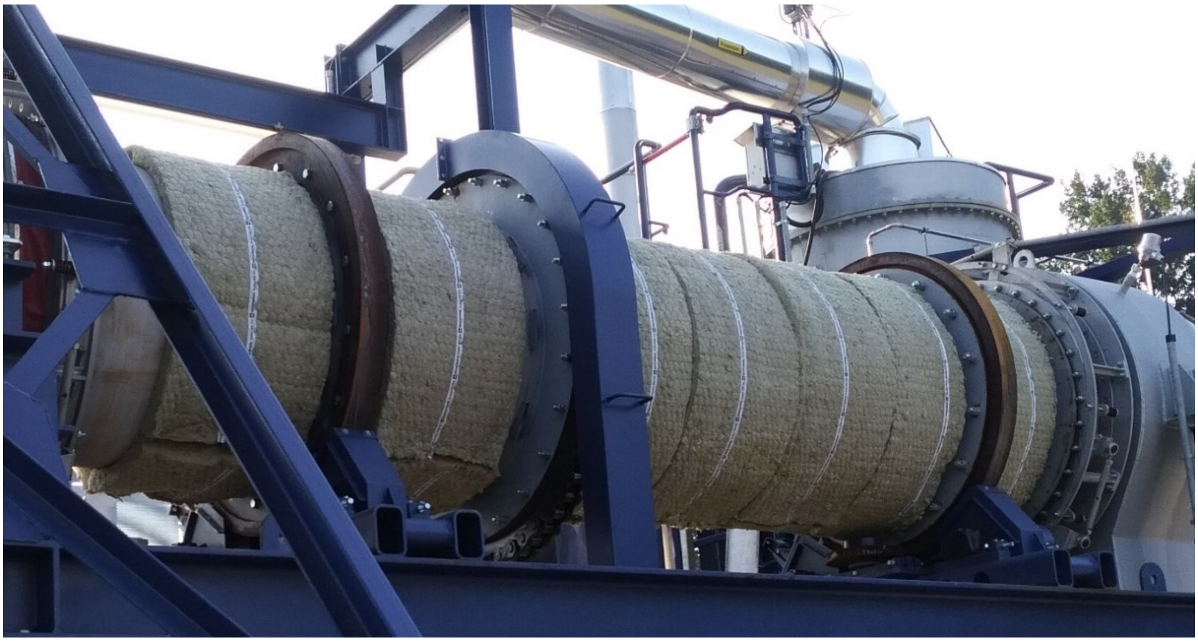


Figure 3.2.8: External isolation (Picture: Emschergenossenschaft/L. Pamuk)

SSA discharge and collection

After the oxidation zone, the SSA was transferred to a BigBag via a discharge screw and a rotary valve, that prevents uncontrolled air intake. The length of the screw conveyor and thus its surface were sufficient to cool down the SSA to ambient conditions *via* radiation losses. If necessary, ambient air could also be blown through the screw, so that the heat transfer was increased and the SSA was further cooled down contactless (Figure 3.2.9).

Figure 3.2.9: SSA discharge at the EuPhoRe®-plant (Picture: Emschergenossenschaft/L. Pamuk)

Heat and energy system

The EuPhoRe®-plant was equipped with two combustion chambers. It is a specific characteristic of the stand-alone plant that the required flue gas was produced in-house and the exhaust gas flow was burned out. With regard to the project time of only 4 years, a pre-drying to 40-45 % dry matter (that would be sufficient for thermally self-sufficient operation) was not implemented. Instead, propane gas burner systems were installed in the two combustion chambers.

An EuPhoRe®-plant would ideally be combined with an (existing) waste incineration to gain synergies with respect to the energy use and the exhaust gas cleaning. At the pilot plant, the two combustion chambers had different purposes.

One of the chambers was responsible to generate sufficient heat and the necessary oxygen demand for the process. The flow of the produced gas was contrarily to the flow of the sludge in the rotary kiln; i.e. maximum temperature and oxygen content was reached in the oxidation zone to guarantee full incineration of all organic compounds. The process was basically controlled by the steering of the combustion chamber, the addition of ambient air to the whole system and the distribution of process gas between the rotary kiln and the gas treatment (see Figure 3.2.10).

The second incineration chamber was responsible for the post-combustion of the exhaust gas. According to the federal emission control ordinance (17. BImSchV), exhaust gas had to be incinerated at 850°C for at least two seconds before final treatment.

The complex interaction of the system had been optimised several times, e.g. with regard to the control of the incinerators.

Figure 3.2.10 a and b: Gas split (flue/exhaust gas) and one of the two incineration chambers (Pictures: Emschergenossenschaft/L. Pamuk)

Exhaust gas treatment

A specific part of the process gas was continuously removed from the system and led to the gas treatment. After the combustion at 850°C, the gas was cooled down with ambient air to approx. 220 °C in order to reduce the thermal stress of the following treatment steps and to precipitate heavy metal compounds which were still in gas phase. After that, an adsorbent ($Ca(OH)_2$; later $NaHCO_3$) was added mainly to fix acid compounds such as HCl and SO_2. Precipitated pollutants were then filtered in a fabric filter (Figure 3.2.11). This retained material was considered as “waste”: it was the sole not recyclable output of the whole process.

Figure 3.2.11 a and b: Inside view of the filter and view of the whole gas treatment system (Pictures: Emschergenossenschaft/L. Pamuk)

After initial setup, the flue gas chimney was equipped with sockets to enable flue gas analyses in conformity with the 17. BImSchV (federal emission control ordinance).

Since the results of the first analyses showed that especially the reduction of the acid components of the flue gas was not sufficient, the control of the filter cleaning process was modified. In addition, the feeding of the adsorbent was optimised. Finally, the type of the adsorbent was changed from $Ca(OH)_2$ to $NaHCO_3$.

3.2.3 Analyses of results of I1 operation

After the setup was completed in April 2019, the plant was operated manually at the beginning due to delays in programming and automatisation. During this period, several optimisation potentials have already been identified and implemented. These aspects have already been described above.

At the beginning of 2020, the operation of the plant was more and more stable. Various continuous trials for some subsequent days and nights have been performed, focusing on (the optimisation of) specific parameters such as the dosing of additives.

Exhaust gas analyses

Exhaust gas has been repeatedly analysed. It turned out that especially the content of acid compound such as HCl or SO_2 was too high with regard to the limits agreed upon with the authority. Using these compounds as an easy-to-measure proxy, the gas treatment was optimised with regard to type and dispersion of the adsorbent and the function of the cloth filter.

It has to be mentioned that the problems related to the gas treatment were related to the uniqueness of the plant, its small size and its features. In full-scale, no comparable problems are expected.

Analyses of input material

In a first stage, the sludge of the WWTP Dortmund-Deusen was used as input material. The sludge was chosen due to its relatively “standard” composition for German sludges with regard to nutrients and pollutants. It is basically a municipal sludge with common industrial influences (Table 3.2.2, Table 3.2.3).

Table 3.2.2: Average composition of sewage sludge of DO-Deusen (main elements)

Main nutrients	**kg/t in OS**	**kg/t in $DS_{23,81\,\%}$**
Total N (N)	11.9	50.0
Total P (P_2O_5)	17.2	72.3
Potassium (K_2O)	0.73	3.05
Magnesium (MgO)	2.58	10.8
Sulfur (S)	2.36	9.90
Alkaline compounds (as CaO)	8.67	36.4

Table 3.2.3: Average composition of sewage sludge of DO-Deusen (heavy metals)

Heavy metals	**mg/kg $DS_{23,9\,\%}$**
Chromium-VI	<0.72
Arsenic (As)	5.3
Lead (Pb)	51
Cadmium (Cd)	0.93
Chromium (Cr)	31
Iron (Fe)	38,000
Copper (Cu)	400
Manganese (Mn)	640
Nickel (Ni)	27
Selenium (Se)	<5.0
Thallium (Tl)	<0.4
Uranium (U)	1.7
Vanadium (V)	21
Zinc (Zn)	880
Mercury (Hg)	0.49

The results of the basic input analyses were repeatedly proven.

Analyses of EuPhoRe®-SSA

Nearto the input substrate (sewage sludge), the P-recyclate (SSA) were regularly analysed in external laboratories for the heavy metal content and nutrient content.

The phosphate-containing SSA produced by the EuPhoRe®-process has the typical red-brown color, which is due to the iron oxide. The residual carbon content is below the detection limit at <0.5 % carbon (C). Fine agglomerates are created that can be easily ground (Figure 3.2.12).

Figure 3.2.12 a and b: EuPhoRe®-SSA quality (Pictures: Emschergenossenschaft/L. Pamuk in (Schmelz et al. 2020)

The first analyses showed that there was a significant heavy metal reduction. Cadmium, mercury and thallium were below the detection limit in all tests (Table 3.2.4). With regard to lead (-70 %) and arsenic (-25 %), good results have already been achieved at temperatures of approx. 850°C, which can be further improved when the desired target temperature of 900 to 1,000°C is reached. All results could be confirmed and replicated in samples taken at different times.

Table 3.2.4: Overview on selected results of the SSA analyses (focussing on heavy metals)

Heavy metals [ppm]	SSA 3 % additive (2020)	SSA 6 % additive (2020)	SSA 3 % (March 2021)	SSA 6 % (April 2021)
As	9	10	10	9,3
Pb	57	35	34	15
Cd	<0,4	<0,4	<0,4	<0,4
Cu	1000	1000	940	780
Ni	74	82	89	65
Zn	1600	1300	2100	1400
Hg	<0,05	<0,05	<0,05	<0,05
Tl	<0,4	<0,4	<0,4	<0,4

In order to achieve significant reductions for copper, nickel and zinc, a temperature of 900 to 1,000°C in the oxidation zone is necessary. Tendencies towards an improved reduction can already be seen in the sample of April 2021 (see Table 3.2.4), related to slightly higher temperatures and an overall stable operation of the kiln.

Table 3.2.5 gives an overview on the nutrient content of the SSA.

Table 3.2.5: Overview on selected results of the SSA analyses (focussing on nutrients)

Nutrients [kg/t; except "N"]	SSA 3 % additive (2020)	SSA 6 % additive (2020)	SSA 3 % (March 2021)	SSA 6 % (April 2021)
N	0,02 %	0,02 %	<0,01 %	0,09 %
K_2O	7,33	7,96	5,93	7,62
MgO	68,1	101	52,4	76,0
S	0,45	0,81	0,42	0,9
CaO	135	177	119	175
P_2O_5	160	153	158	154

Pot trials with EuPhoRe®-SSA

A representative sample of the EuPhoRe®-SSA had been sent to an external company in late summer 2020 to test the plant availability of its phosphorus. Final results of the pot trials were delivered in mid-2021.

The main results are shown in Figure 3.2.13 and Figure 3.2.14. A significant difference of the dry matter development of a specific cut is given if small letters ("a", "b", …) are different; e.g. in case of the first cut of ryegrass, a significant difference was given for the zero control, the two EuPhoRe®-SSA and TSP, whereas the difference of 3%- and 6%-EuPhoRe®-SSA was not significant. Both in the case of ryegrass and in the case of alfalfa, the dry matter development using EuPhoRe®-SSA was significantly higher compared to the zero control, thus proving the efficacy of the EuPhoRe®-SSA as a fertiliser.

Compared to the reference (triple super phosphate; TSP), the biomass development was lower, mainly related to the "rapid" bioavailability of the (water-)soluble P-fractions of TSP. In contrast, the EuPhoRe®-SSA has to be addressed as a slow release fertiliser. In the long term, it can be expected that the differences to TSP are balanced.

Comparing the EuPhoRe®-SSA with 3% $MgCl_2$ and 6% $MgCl_2$, the differences were small. A slight tendency towards an increased biomass growth with 6% $MgCl_2$ can be seen for ryegrass (HGoTech GmbH 2021), which is expected.

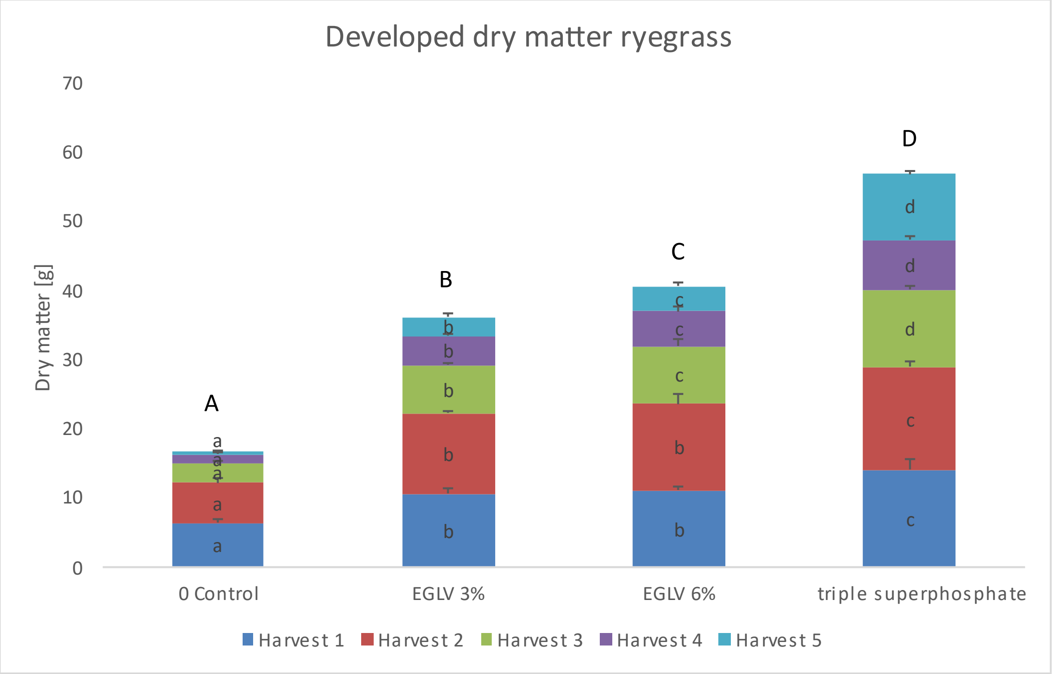


Figure 3.2.13: Dry matter development for 5 harvests of perennial ryegrass, comparing EGLV 3% and 6% as compared to TSP and zero control. Graph shows means and standard deviations (=5), different letters indicate significant differences (Duncan-Test, α=0,05). Upper case letters: sum of total biomass over 5 harvests, lowercase letters compare values for each individual harvest (HGoTech GmbH 2021)

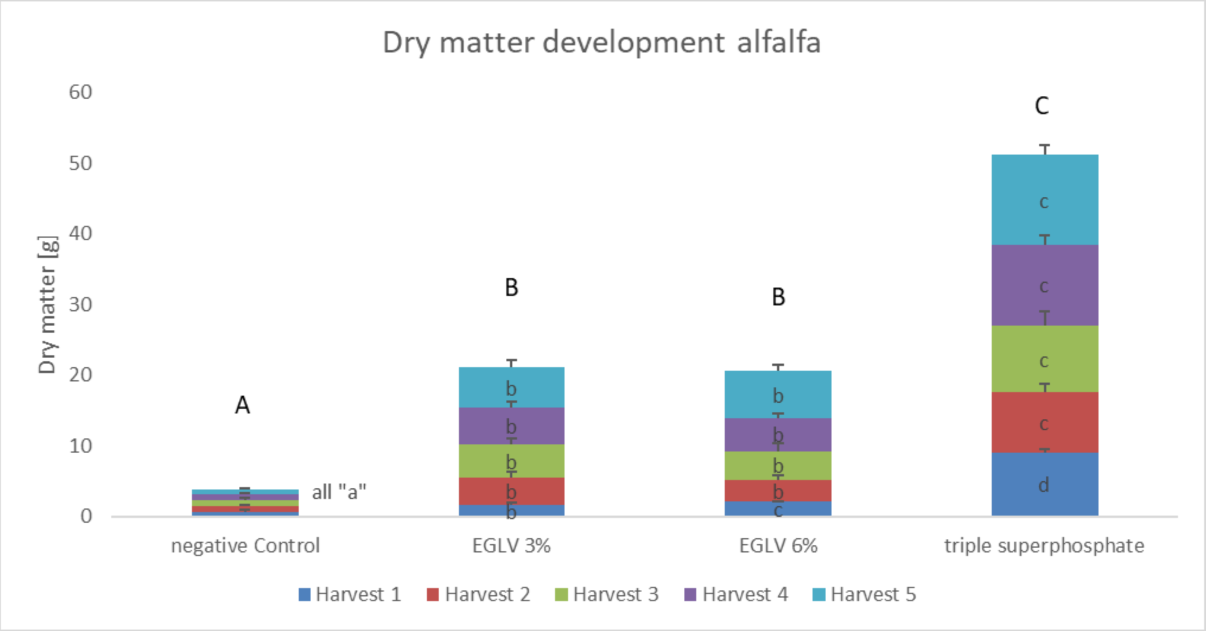


Figure 3.2.14: Dry matter development for 5 harvests of perennial alfalfa, comparing EGLV 3% and 6% as compared to TSP and zero control. Graph shows means and standard deviations (n=5), different letters indicate significant differences (Duncan-Test, α=0,05). Upper case letters: sum of total biomass over 5 harvests, lowercase letters compare values for each individual harvest (HGoTech GmbH 2021)

Further, the EuPhoRe®-SSA underwent extensive quality assessment tests within the quality assessment work package of Phos4You (Bogdan et al. 2021).

Grinding and granulation of EuPhoRe®-SSA

With regard to the full-scale use of the produced SSA, EG made contact to a fertiliser mixing company to plan full-scale tests. Due to the ongoing optimisation process, a sufficient amount of SSA with a constant quality (approx. 15 -20 tonnes is needed) could not have been produced at the time of the report redaction. Independently of the full-scale use of the SSA within a fertiliser mixing process, the SSA were delivered to a grinding and to a pelleting company to assess the specific properties of the EuPhoRe®-SSA with regard to the fertiliser processing steps.

The grinding tests showed that the intended grain size (retention < 2% in 90 micrometer-sieve) could be easily reached. Due to the small ash sample ("only" 400 – 500 kg), the abrasive effect of the ash on the mills/machines could not be determined finally. Based on the first experiences, it can be assumed that abrasive effects are small (Lösche GmbH 2021).

A small amount of the ground material was processed to fertiliser pellets, using salt solution as binding agent. The results are shown in Figure 3.2.15. Size and size distribution of the pellets was regular. Subsequent tests showed that the stability of the pellets is suitable for the use in common agricultural equipment such as centrifugal fertiliser spreaders (Eirich GmbH & Co KG 2021).

Figure 3.2.15: Pellets of EuPhoRe®-SSA and 2 different types of salt-solution*LCA for I1***

The EuPhoRe®-process has been included in the LCA-LCC works done within Phos4You (cf. chapter 5).

3.2.4 Discussion of results for I1 operation

Due to the ongoing (technical) optimisation of the plant as a whole and thus, the (so far) limited results of steady operation of the plant, the complex interactions of sludge input, plant operation (e.g. temperature), additives and SSA quality could not have been completely assessed at the time of report redaction. Nevertheless, it is already clear that it is possible to create a sewage sludge SSA a) that has a notably reduced heavy metal content and b) that contains nutrients (especially P) which are plant-available.

These results are basically valid for the input material used so far (i.e., a municipal sludge with an average composition). The “limits” of the EuPhoRe®-process could not yet be assessed, but given a steady, optimised operation of the plant, it is expected that result could be repeated for e.g. sludges with a higher heavy metal content.

Even if the plant would (in full-scale) ideally be combined with existing technologies (e.g. using surplus energy / exhaust gas treatment of e.g. a waste incineration plant) – thus avoiding some of the problems observed – the experiences gained during setup, start-up, operation and optimisation can be regarded as an important result of the project.

The stand-alone concept of the pilot plant is generally transferrable to other (larger) WWTP. In this case, an upscaling would be needed. During this process, the exhaust gas treatment would certainly be revised and optimised, using standard components of the exhaust gas treatment technology, because this down scaled part of the system turned out to be prone to failures.

During upscaling for the installation of a permanently operated sewage sludge treatment plant, the high temperature of the flue gas would not be cooled down with ambient (as it is the case at the pilot plant). Instead, standardized energy recovery systems would be used. The recovered energy would then be used for pre-drying so that thermally self-sufficient operation is guaranteed.

3.2.5 Conclusion for I1

It could be shown that the EuPhoRe®-process is suitable for a two-stage thermochemical treatment of sewage sludges. Produced SSAs after appropriated granulation or dust binding generally meet the requirements for phosphate fertilisers, notably in regard to the heavy metal content.

Specific aspects regarding the evolving legislation are detailed within the final report of Phos4You (Ploteau et al. 2021). Problems observed were related to the size of the plant ("demonstrator") and will likely not occur in full-scale.

The EuPhoRe®--processes considered in Phos4You will be implemented on an industrial scale in Mannheim, Germany (Franke 11/22/2017) in 2021(sludge input capacity 135,000 tonnes/a). Other full-scale realisations are under discussion (Klose 8/3/2021).

3.3 Demonstrator I6.1: Bio-acidification before P precipitation from sludge (optimised Struvia™)

Authors: Marie-Line Daumer, Younes Bareha (INRAE); Fabien Vedrenne, Marisa Cunha, Cédric Mébarki (Veolia)

The aim of the I6 demonstrator was to demonstrate the STRUVIA™ technology of Veolia in different new applications, enabling implementation and testing solutions to recover P from sewage liquor. The STRUVIA™ technology had been developed by Veolia during the P-REX European project and validated for P-recovery as Struvite on sludge liquor after digestion, which is leading to 20 % recovery of the total P entering in a municipal WWTP. The objective was to make the demonstration of a bio-acidification stage on liquid sludge (developed by INRAE) combined with a STRUVIA™ unit to crystallise the P-PO_4 released into a P by-product. This combination was proven in labs to significantly increase the P-recovery rate.

3.3.1 Preparation of I6.1

The results presented in this chapter are those necessary to design and run the demonstrator. More detailed results have been already presented in conferences and discussed in three scientific papers. The first one has been published in Environmental technology (Bareha et al. 2020), the further are under revision or preparation. They will help to understand better the mechanisms involved at the different steps and will be useful to optimise the operation of the process.

3.3.1.1 *Feasibility of P dissolving when Al-salts were used for P removal*

The first site to test was Marquette-lez-Lille. It’s a large scale WWTP combining biological and chemical P removal (EBPR + Aluminium salts). It was chosen because of the pressure on the land to spread the sludge.

In order to decide where the demonstrator should be implemented five sludge were sampled at different stages of the WWTP and tested for their Biological Phosphorus Dissolution Potential (BPDP) with bio-acidification test as previously described by Braak et al. 2016.

The characteristics of the sludge are presented in Table 3.3.1.

Table 3.3.1: Sludge characteristics within the BPDP test (TS: total solid, MS: mineral solid)

	Secondary sludge	Thickened secondary sludge	Thickened primary sludge	Thickened mixed sludge	Digested sludge
TS (g.kg^{-1})	5,2±0,1	60±1	63±1	59±1	58±1
MS (g.kg^{-1})	1,8±0,2	15±1	28±1	21±1	21±1
P total (mg.kg^{-1})	190±5	2747±135	1133±12	1849±54	1799±9
Fe total (mg.kg^{-1})	41±1	370±10	732±9	585±8	474±13
Al total (mg.kg^{-1})	48±2	595±17	820±20	604±67	560±1
Ca total (mg.kg^{-1})	339±20	3729±107	3569±460	2717±237	2086±1
Mg total (mg.kg^{-1})	65±4	700±20	323±40	453±0	389±1
Cu total (mg.kg^{-1})	1,5±0,1	20±1	20±2	19±1	
Zn total (mg.kg^{-1})	6±1	81	101±1	89±4	89

The initial dissolved P was very high (25 to 45 %) compared to other sludge from similar WWTP (usually less than 10 % of total-P). The transport was involuntary performed without temperature control during summer and took 48 hours instead of the 7 hours expected. That could explain that the biological release could start with the volatile fatty acid (VFA) produced by acidification induced by the endogenous carbon available in sludge.

As the optimum DM for the lab-test with our equipment is around 30 g.Kg^{-1}, the sludge to be tested were ½ diluted with secondary sludge before thickening (thickened secondary sludge (M1), thickened mixed sludge (M2) and digested sludge (M3)).

The Table 3.3.2 presents the characteristics of the mixture used for the acidification test.

Table 3.3.2: Characteristics of the mixture used for the acidification test

	M1	M2	M3
TS (g.kg^{-1})	33	32	22
MS (g.kg^{-1})	8	11	10
P total (mg.kg^{-1})	1469	1020	782
Fe total (mg.kg^{-1})	201	313	303
Al total(mg.kg^{-1})	322	326	285
Ca total (mg.kg^{-1})	2034	1528	1173
Mg total (mg.kg^{-1})	383	259	174
Cu total (mg.kg^{-1})	11	11	9
Zn total (mg.kg^{-1})	44	48	38

After the bio-acidification test, the pH was close to 4 in M1 and M2 but only 4.7 in the digested sludge (M3). Dissolved P varied from 65 % of the total-P for the thickened secondary sludge (M1) and for the digested sludge (M3) to 69 % for the mixed sludge (M2) (Table 3.3.3). It was 65 % for the thickened secondary sludge (Table 3.3.3). The difference between digested and not digested sludge could be due to the pH. These results are in accordance with previous works (Braak et al. 2016). The repeatability of the tests was good (less than 5 % of variation between the 3 repetitions) as the reliability of the results confirmed by the P mass balance between 92 and 108 %. The low aluminium dissolution has shown that a large fraction of P in sludge was stored in the biomass because of the EBPR process and/or precipitated as Irons salts.

Table 3.3.3: Concentrations after acidification (concentrations of total and dissolved phosphorus are in $mg.l^{-1}$)

		N	**P**	**Ca**	**Mg**	**Fe**	**Al**	**Cu**	**Zn**
M1	total	2500±100	1468	2034	383	205	307	11	43
	Dissolved initial	52	443	206	132	nq	nq	nq	nq
	Dissolved final	72±3	961±1	589±25	222±12	114±8	34±2	nq	nq
	% Dissolved final	**3**	**65**	**29**	**58**	**56**	**11**	**0**	**0**
M2	Total	2100±100	1020	1528	259	313	326	11	48
	Dissolved initial	145	463	372±1	243±1	11±1	nq	nq	nq
	Dissolved final	181	701±14	764±30	227±5	132±12	36±5	nq	nq
	% Dissolved final	**9**	**69**	**50**	**88**	**42**	**11**	**0**	**0**
M3	Total	800±100	782±8	1173±22	174±4	303±12	285±16	9±1	38±1
	Dissolved initial	145	161	101±1	19±1	15±1	nq	nq	10±1
	Dissolved final	177	510±17	909±37	151±14	69±2	22±1	nq	nq
	% Dissolved final	**22**	**65**	**77**	**87**	**23**	**8**	**0**	**0**

After the acidification step, 77±1 % of the mass for M1, 82±1 % for M2 and 86 % for M3 was recovered as liquid phase by centrifugation. Therefore, the final P-recovery rate in the liquid was 51 to 56 % in the three products (Table 3.3.4). As struvite or calcium phosphate precipitation is usually close to 100 %, those rates would be close to the final recovery rate of the process if it is applied before anaerobic digestion.

Table 3.3.4: Recovery of each element in the liquid phase (%). (C= control)

	P	Ca	Mg	Fe	Al
M1-C	32	42	47	7	6
M1	51	72	67	42	9
M2-C	39	9	53	4	1
M2	56	54	65	34	8
M3-C	17	9	13	8	9
M3	51	60	64	19	8

Finally, the large amount of calcium in the liquid compared to Iron or Magnesium should favor calcium phosphate precipitation (Table 3.3.5). If the low dissolution of metallic compounds, excepted Iron, would be confirmed by further trials, they should not interfer with phosphate recovery.

Table 3.3.5: Final concentration in liquid fraction after bio-acidification (in mM)

	N	P	Ca	Mg	Fe	Al
M1	5	31	15	9	2	1
M2	13	23	19	9	2	1
M3	13	16	23	6	1	1

This first experimental set confirmed the feasibility of implementing a combined bio-acidification + Struvia™ process in WWTP using EPBR + aluminium salts for P removal.

No significant differences were observed on P-recovery in the liquid between the different types of sludge excepted that the pH reached at the end of the bio-acidification test was higher in the digested sludge.

3.3.1.2 *Location of the P-recovery process and parameters for designing the pilot*

A second experimental set was designed with three objectives

- To be sure that the bad transport conditions had no impact on the final results
- To definitely choose the best location (before or after anaerobic digestion)
- To define the hydraulic retention time (min and max) to guaranty a low pH

A comparison with chemical acidification (CPD) was also performed to better understand the mechanisms of dissolution. For that, HCl 37 % was added either directly in the sludge to reach pH 4 and pH 2 or after bio-acidification to reach the same pH.

The sludge sampled were the thickened mixed sludge (MS1) and the digested sludge (DS1)

Characteristics of the sludge are presented in Table 3.3.6. The TS of the sludge was lower than the first sampling, therefore no dilution was applied.

Table 3.3.6: Characteristics of sludge used for the second bio-acidification experiment (raw matter basis)

	TS	**VS**	**MS**	**TKN**	**NH4+**	**Total P**	**Total Fe**	**Total Al**
	(g.kg^{-1})				**(mg.kg^{-1})**			
MS1	37±1	27±1	10±1	2,3±0.1	245±2	939±26	636±9	473±5
DS1	33±1	19±1	13±1	2,9±0.1	1177±40	1155±32	574±25	540±37

What is the best location for the demonstrator (before digestion or after the first digestion step)

As noticed on the Table 3.3.7, to get to pH = 4±0,5, more than twice the amount of acid and plus 52 % of sugar for DS1 than MS1 to reach pH 4+/-0.5 is needed.

Table 3.3.7: Amount of acidification agent required to reach pH = 4±0,5

	Sugar		HCl 37 %		
	g_{sugar}/ kg_{sludge}	pH min (after 24h)	l/t	g_{HCl}/Kg_{sludge}	pH_{min}
MS1	11,6	4,1	5,2	2,0	4,1
DS1	17,7	4,6	11,9	4,4	4,1

From these results, the demonstrator would be best located before anaerobic digestion.

What is the required range for Hydraulic retention time?

In non-digested sludge, the pH min was reached after 24 hours with bio-acidification and increased after 48 hours. The maximum P dissolution was reached after 48 hours, remained stable for two days more and then decreased. Bio-acidification was as efficient as chemical acidification for P dissolution (Figure 3.3.1). The P dissolution rate was only 35 %. That could be explained by the higher Al/P molar ratio in sludge in this experiment (0,6) compared to the first one (0,3).

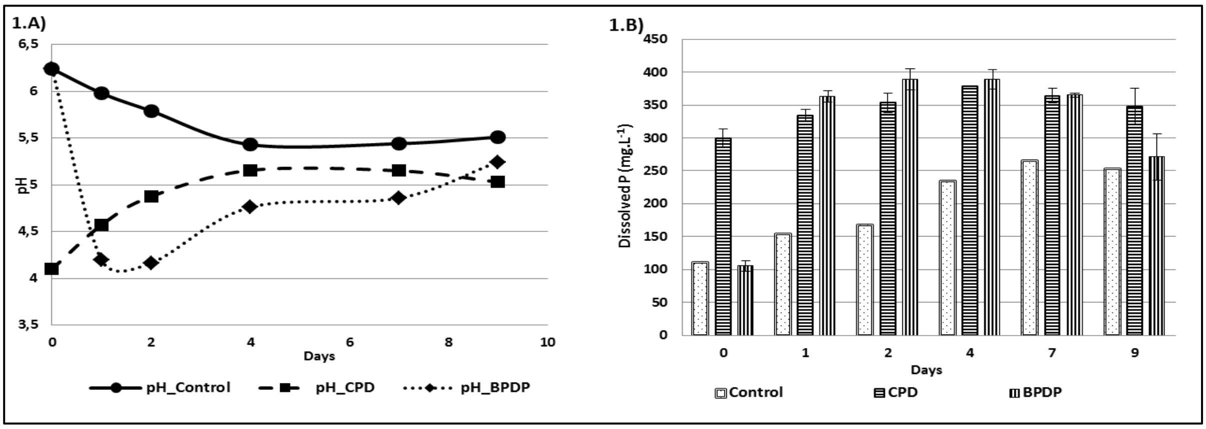


Figure 3.3.1: pH evolution and P dissolution in non-digested sludge (CPD: chemical P dissolution, BPD: biological P dissolution)

In digested sludge, despite the higher amount of sugar added, the lowest pH was only 5. It was reached after 24 hours and remained stable for 2 days. The higher P dissolution was reached after 24 hours (Figure 3.3.2).

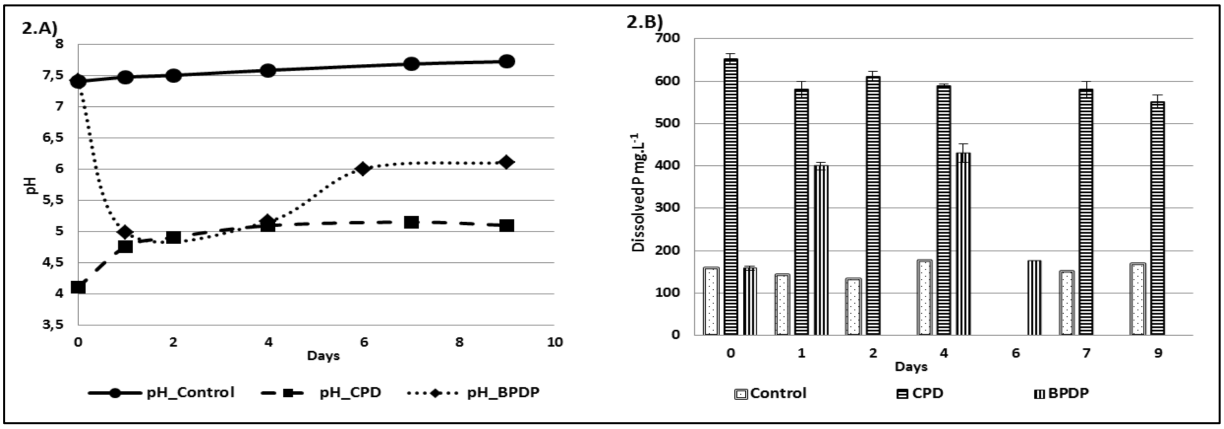


Figure 3.3.2: pH evolution and P dissolution in digested sludge (CPD: chemical P dissolution, BPD: biological P dissolution)

A hydraulic retention time between 24 and 48 hours seems to be sufficient (to be confirmed with industrial co-substrates).

Is a Fe removal module needed?

Iron dissolution during bio-acidification was much more efficient in non-digested sludge than in digested sludge (56 % and 18 % respectively). It is higher than chemical dissolution at pH 4 (45 %) and comparable to the level reached at pH 2 (57 %) (Table 3.3.8).

Table 3.3.8: Fraction of total Iron in liquid after biological (BPDP) or chemical (CPD) acidification at different pH level. Data expressed in %.

		BPD	CPD
MS1	Max (pH)	56 (4,1)	
	pH 4	45	48
	pH 2	57	nd
DS1	Max(%) (pH)	18 (5,2)	
	pH 4	24	25
	pH 2*	48	48

*To reach pH, 2 acid was added after the BPD

As the Iron concentration in sludge is high, it could be necessary to remove Iron from the liquid before P crystallisation when non-digested sludge is chosen. This option will depend on the quality of the recycled P product required.

3.3.1.3 *Choice of the co-substrate*

For this experiment, only non-digested mixed sludge (MS2) and non-thickened biological sludge were sampled.

Because of the high TS content of MS2, the BPD was studied on non-digested mixed sludge (MS2) and on MS2 diluted with non-thickened sludge (0.5 % dry matter) (MS3). It was also an opportunity to evaluate the effect of the TS content on the BPDP of sludge at lab-scale and to be sure that the mixing rate which can be affected by the TS content did not modify the results.

Sludge characteristics are presented in Table 3.3.9.

The initial pH of MS2 (5.62) and MS3 (5.88) in this experiment was lower than the pH of MS1 (6.24) which made the initial dissolved-P higher (30 % ±2 in MS2/MS3 compared to

11 % in MS1). There was no significant change in pH and dissolved P percentage after dilution.

Table 3.3.9: Characteristics of the sludge used for the bio-acidification (raw matter basis)

	TS	VS	MS	TKN	NH4+	Total P	Total Fe	Total Al
	(g.kg^{-1})				(mg.kg^{-1})			
MS2	55±1	39±1	15±1	2.8±0.1	351±13	1237±26	527±7	641±1
MS3	30±1	22±1	8±1	1.7±0.2	181±2	715±37	281±11	352±5

The first co-substrate used in this experiment is a modified industrial starch sold for a denitrification purpose (Cos1) and the second one is a by-product of food additive (Erythrol) manufacture (Cos2) that can be found in abundance and at low cost, near the WWTP. To be able to compare the results to the previous one, the BPDP using sugar was also performed. In every case the co-substrate was added at 0.5 g COD.g VS^{-1}. A control sample of the sludge without any addition was also studied to investigate the natural P release by PAOs.

MS2 and MS3 have similar pH and dissolved P evolution, especially after 20h of incubation. The pH decreased to pH 4.3 when using sugar, and to pH 4.7 and pH 4.1 when adding Cos1 for MS2 and MS3 respectively. When using Cos2, the pH of MS2 and MS3 dropped only to pH 5.2 and pH 5.3 respectively. The pH remained stable in the control sample. The P dissolution rate was 43 % to 45 % of total P with sugar, 36 % to 38 % with Cos1 and 37 % to 40 % with CoS2. The pH in MS2 and MS3 continued to decrease to pH 4.3 and pH 3.8 after 40 h respectively when Cos1 was used, remains stable or re-increased slightly with Cos2 (Figure 3.3.3 and Figure 3.3.4).

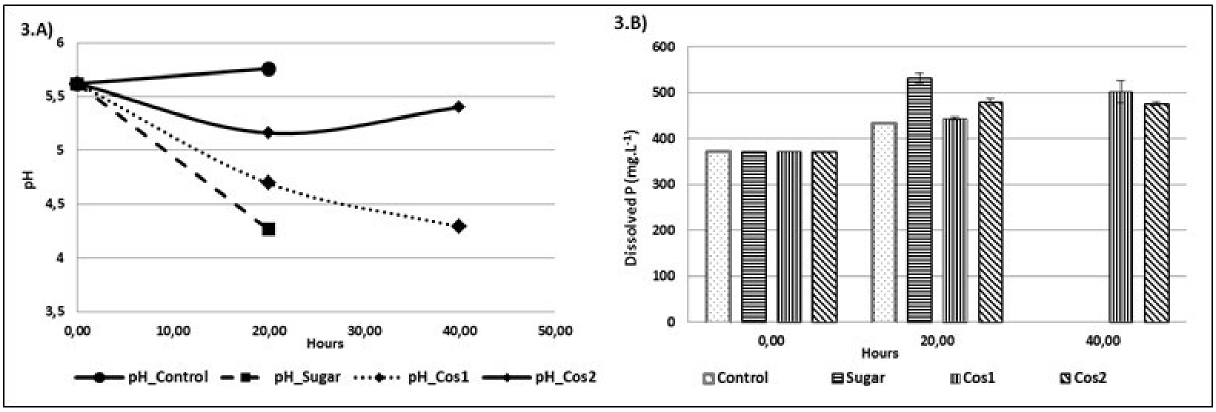


Figure 3.3.3: pH evolution and P dissolution in MS2 with different co-substrate (Cos1: modified starch, Cos2: Erythrol)

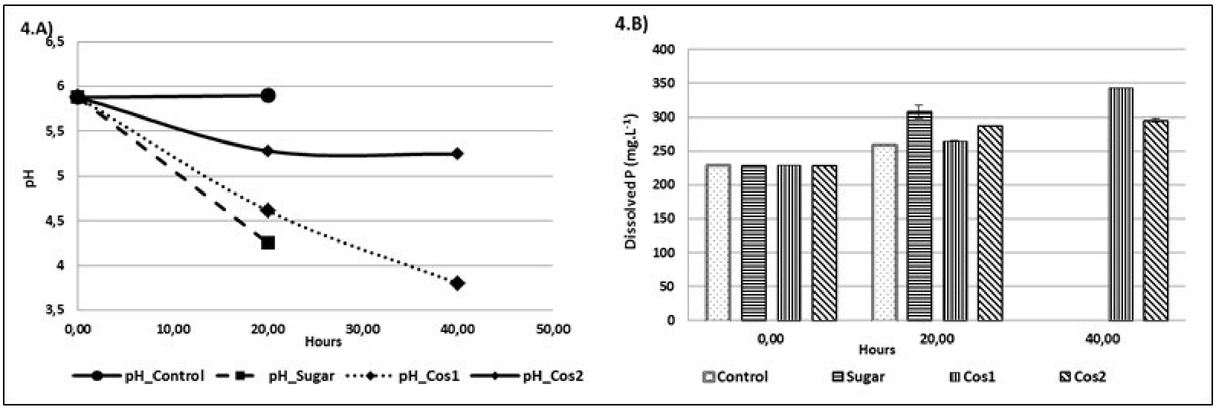


Figure 3.3.4: pH evolution and P dissolution in MS3 with different co-substrate (Cos1 : modified starch, Cos2: Erythrol)

The TS content of the sludge did not affect significantly the bio-acidification step.

To see if a higher amount of Cos2 could decrease the pH down to 4 and therefore increase the P dissolution, a new trial was performed with MS2 sludge stored for about one month, at 4°C in a concealed container. During this storage, the pH slightly increased from 5.6 to 5.9 decreasing the dissolved P by only 2 %. The BPDP with two concentrations of Cos2 (0.75 and 1 g COD.g VS^{-1}) were compared with Cos1 (0.5 g COD.g VS^{-1}). The pH decreased to 5 and 4.9, with Cos2 at 0.75 g COD.g VS^{-1} (35 g Cos2.kg MS2^{-1}) and 1 g COD.g VS^{-1} (47 g Cos2.kg MS2^{-1}) respectively, when it decreased to pH 4.16 when Cos1 was used at 0.5 g COD.g VS-1 (24 g Cos2.kg MS2^{-1}). However, as for the first trial with those co-substrates even if the pH was higher there was no difference between P dissolution rate (48 %) with CoS2 and CoS1.

Finally, a last test was performed with a new co-substrate (CoS3: fruit industry waste) and compared to Cos1. Mixed thickened sludge was sampled in the WWTP (MS4). Sludge characteristics are shown in the Table 3.3.10. The initial pH was the same as for MS2 (5.6) but the initial dissolved P rate was higher (42 %) probably because of the low Al/P ratio (0,3).

Table 3.3.10: Characteristics of the sludge used for the bio-acidification with Cos3 (raw matter basis)

	TS	**VS**	**MS**	**TKN**	**NH4+**	**Total P**	**Total Fe**	**Total Al**
	(g.kg^{-1})				**(mg.kg^{-1})**			
MS4	37±1	26±1	11±1	2.8±0.1	351±13	783±26	433±12	205±3

The minimum pH reached with CoS3 was 3.8 after 24h and decreased linearly to 3.3 for the next 8 days. This is lower than the minimum reached with CoS1 (4.1).

With CoS 3 The dissolved P rate was 67 % after 2 days and after a short decrease increased up to 76 % after 10 days. With CoS1 the maximum dissolution rate was reached after 3 days (67 %).

The feasibility to use industrial by-products as co-substrates was proven and the CoS3 was chosen for the demonstrator in Lille.

After this first preparation step the demonstrator could be designed (see next chapter).

In preparation of the moving of the pilot to Tergnier which is a small WWTP using Iron chloride for P removal, labscale work was going on to define more precisely the parameters for Iron recovery from the liquid phase. An assessment of the side impacts of the P-recovery process on the biogas production from anaerobic digestion of sludge and reduction of land for sludge or digestate spreading was also performed.

3.3.1.4 *Iron removal (recovery?) from the liquid phase*

Six different cationic exchange resins were tested to remove Iron from the liquid after bio-acidification of sludge (Table 3.3.11). For each of them, 5 amounts with two contact time (15-30 min.) were tested.

Table 3.3.11: Characteristics of the resins tested

Resin	Fonctionnal group	Form	pH	Regeneration
IRC 747	aminophosphonic	Na^+	2 - 4.5	HCl 1 à 2N
IRC 748	Iminoacetic acid	Na^+	1.5 - 14	HCl 5 à 10 %
IRC 83	Carboxylic acid	H^+	6 - 14	HCl 5 à 10 %
HPR 1100	Sulfonic acid	Na^+	1 - 14	HCl 5 %
TP207	Iminodiacetic acid	Na+	0-14	HCl 7 %
IR 120	Sulfonic acid	H^+	0 - 14	HCl 5 à 8 %

IRC747 (20g.L^{-1}-30 min), IRC 748 (50g.L^{-1}-15min), TP 207 (50g.L^{-1}-15 min.) were the most efficient with more than 95 % of Iron trapped.

The resins removed also some others cationic compounds as shown in Table 3.3.12.

Table 3.3.12: Cations removal by the resins (% of the initial concentration)

%	Fe	Mg	Ca	Al
IRC747	97	90	88	93
IRC748	96	97	98	87
TP207	95	93	70	73

Probably because of its aminophosphonic group, the IRC 747 is also increasing slightly the P concentration (+11 %).

The resins are also removing calcium and magnesium. It could be an advantage to obtain a purer salt from the crystallisation step. It could also be an inconvenient because more reactant will be required to obtain P precipitation and the resins will be saturated more rapidly.

During the regeneration the best results were obtained with IRC748 with 98 % of Iron recovered in the solution in only 2 cycles.

The cost of IRC748 is also twice as cheap as the TP207.

After regeneration the solution is containing also magnesium and calcium. The impact of using back this solution to remove P in the WWTP has to be assessed. Regeneration has still to be improved to be able to use the regeneration solution as reactant for P removal instead of Iron chloride.

3.3.1.5 *Effect on biogas production*

An experimental set combining bio-acidification, separation, Iron removal, P crystallisation as struvite and biochemical methane potential (BMP) has been performed at lab scale. The BMP tests were done on the effluent of the crystallisation unit, the acidified sludge, the mix of these two products in the same ratio as on the process (Mix1) and on the mix with just enough liquid to increase the pH up to 6 (Mix2).

The co-substrate added for bio-acidification of sludge is a very concentrated carbon source. Mixing this co-substrate mixed with sludge even without bio-acidification would increase the methane production by 60 %.

During the bio-acidification, sugar from the co-substrate is converted to lactic and other organic acids, which are not kept during the crystallisation process, thus increasing the methane production of the acidified sludge mixed with the liquid from crystallisation by 16 % compared to the mix of sludge and co-substrate without bio-acidification. Hydrolysis of sludge by the acidic phase could explain this difference.

The methane production in relation with the fresh matter was increased again by 9 % when only the amount of liquid to increase the pH of acidified sludge from 4 to 6 is added. The high BMP of acidified sludge compared to the liquid is explaining this result since the acidified sludge mass ratio is increased (Figure 3.3.5). The liquid in excess could be used for denitrification purpose and the volume of the digester could be reduced.

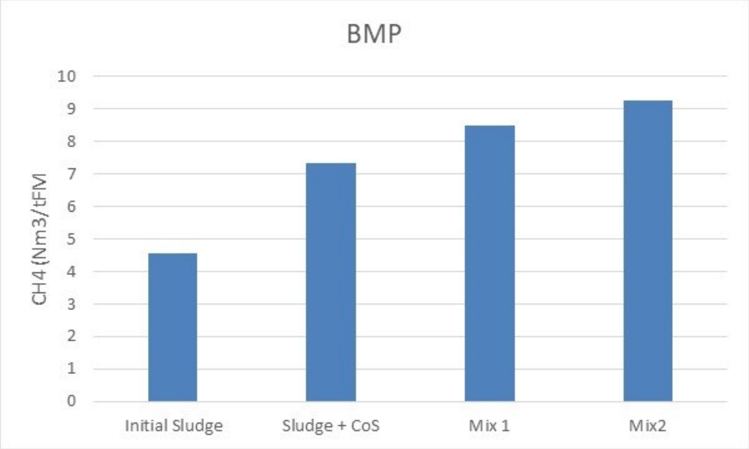


Figure 3.3.5: Biochemical methanogenic potential of acidified sludge compared to initial sludge (FM: fresh matter).

Finally, the methane production with the P-recovery process could be twice as much than with WWTP sludge only, balancing a part of the cost of this process.

These results obtained with BMP should have been confirmed at pilot scale in an anaerobic digester running continuously with the products of the demonstrator. Unfortunately, COVID has stopped the experiments and as the demonstrator was not running anymore it was not possible to store the sludge in good conditions to perform the experiments after the confinement.

3.3.1.6 *Effect on sludge spreading*

From the results of the last experiments the land surface required to spread the digestate with and without the P-recovery process on the basis of 170 kgN.ha^{-1} and 50 kgP.ha^{-1}were calculated.

Before the process, P was the limiting factor and the maximum amount for digestate spreading was 50 m^{3}.ha^{-1}. After, N was the limiting factor and it is possible to spread 85 m^{3}.ha^{-1} (drop of 40 % in land required). Copper and zinc were under the regulation limits.

3.3.2 Execution of I6.1

In order to upscale the lab work previously done, the Marquette-lez-Lille WWTP welcomed the demonstrator. The demonstrator was implemented on the sludge line Figure 3.3.6.

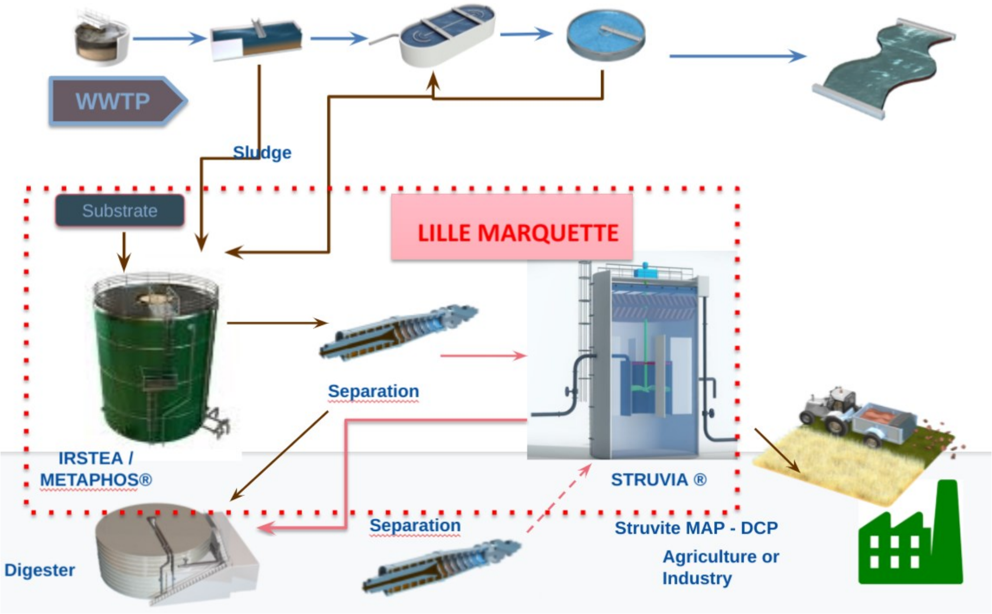


Figure 3.3.6: Perimeter of implementation of the demonstrator in the Marquette-Lez-Lille WWTP (Source: Veolia)

Later, due to a forced move and aluminium causing lower performance, the pilot was located in Tergnier to finalize the demonstration of the P recovery performance.

Schemes of the pilot used in Lille and Tergnier are in Figure 3.3.7. The volumes of tanks were adapted for each plant but with the same operability.

The thickened sludge feeds the bio-acidification tank that is dedicated to the release of Phosphorus. A recirculation loop makes it possible to monitor the temperature, the pH and the oxidation-reduction potential.

The bio-acidified sludge goes through a solid-liquid separation step. The solid part goes to the digester. The liquid part is stored in a buffer tank before going through a polishing step for metals removal (ion exchange resin - OPALIX type unit).

The effluent deprived of pollutants enters the precipitation process STRUVIA™ (also called SAPHIRA) where reagents are added. Depending on the final P product required, a magnesium or a calcium-based chemical is dosed. If required, NaOH is also dosed to adjust the pH. The liquid effluent deprived of phosphorus goes to the digester. The precipitates are recovered.

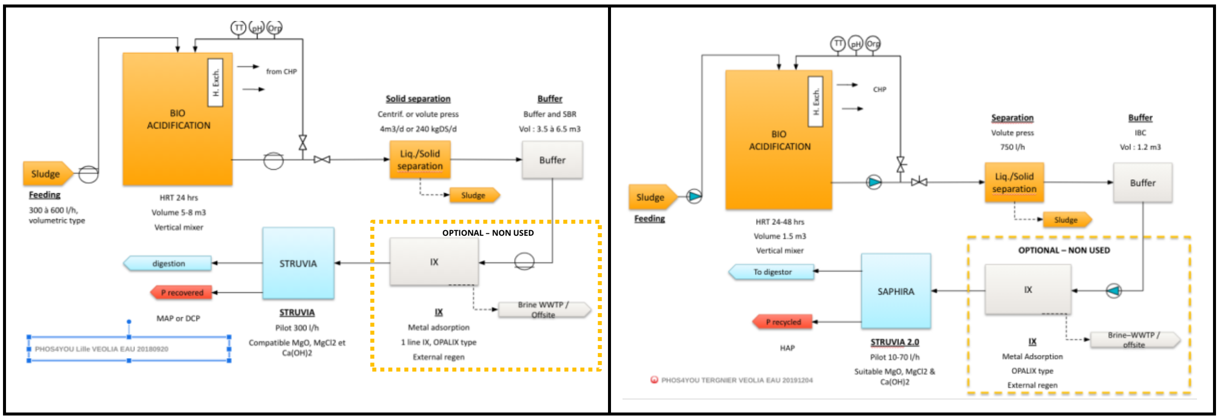


Figure 3.3.7: Scheme of demonstrator in Lille (left) and Tergnier (right); (©Veolia)

Pictures of both places are gathered in Figure 3.3.8.

In Marquette-lez-Lille

In Tergnier

Figure 3.3.8: Both sides of the demonstrator in each location, Lille and Tergnier (©Veolia, Cédric Mébarki)

The operating parameters of the demonstrator were based on the preparatory tests. Table 3.3.13 summarizes the sequence of tests carried out in Lille. The objective was to modulate two factors: the Co-substrate dose and the retention time.

The chosen co-substrate came from a candied fruit production plant. The non-purity of this waste explained the differences between the expected ratio and that actually measured. The differences were known and the whole range of ratios, from 1 to 2, was studied. The first two tests were carried out without cosubstrate. The following ones with real ratios between 1 and 2.5 g COD/g VS.

The retention time of the first two trials covered the range 21-64h. All the tests with co-substrate took place in a range of 20 to 43 hours.

Table 3.3.13: Sequence of tests carried out in Lille.

day	Expected Cosubstrate dose (g/g VS)	Real Cosubstrate dose (g/g VS)	Final batch volume (m3)	Remaining volume (m3)	Added sludge (%)	retention time (h)	Pressing day
29-Jun	0	0	2,868	1	65,13	64	2-Jul
3-Jul	0	0	2,132	1,284	39,77	21	4-Jul
5-Jul	1	1,07	2,408	1,58	34,39	20	6-Jul
9-Jul	1	1,24	2,52	1,612	36,03	43	11-Jul
12-Jul	1,3	1,49	2,6	1,632	37,23	26	13-Jul
16-Jul	2	2,48	2,65	1,594	39,85	42	18-Jul
23-juil	1,5	2,08	3,194	1,594	50,09	22	-
24-Jul	1,8	2,4	3,194	1,594	50,09	43	25-Jul
26-Jul	1,8	1,67	3,624	1,594	56,02	21	27-Jul

In Tergnier, the inlet sludge concentrations were heterogeneous, mostly due to the lack of a separate network. Sugar dosing rate was in a narrower range than Lille with values from 1 to 1.3 g COD/VS of "active" material. Thirteen successive batches were carried out.

3.3.3 Analyses of results of I6.1 operation

In Lille, total phosphorus was analysed internally and externally on the inlet sludge (SP1). The dissolved phosphorus was measured on the acidified sludge (SP2) and on the centrate (SP3) (Figure 3.3.9).

The inlet sludge had fluctuating values. From one sample to another, they were heterogeneous, this was due to the fact that their composition was a mixture of primary, biological and a variable fraction of sludge from the stormwater line. The pH of the inlet sludge was between 5.5 and 6, so it was likely that the acidification of the sludge has started before it passed through the bio-acidification tank.

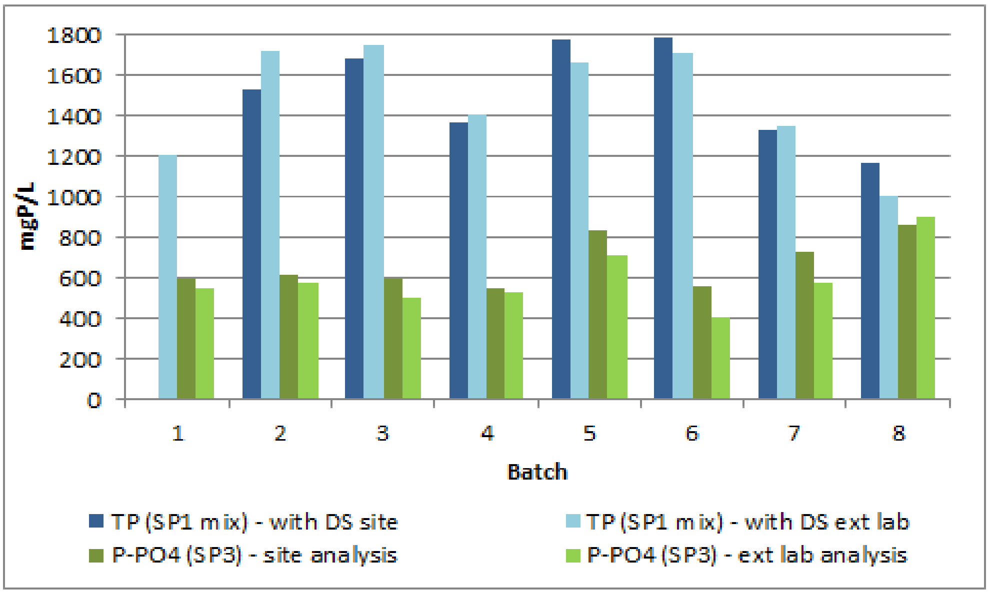


Figure 3.3.9: Phosphorus concentration (total and dissolved) on Lille demonstrator

Bio-acidification reached up to 800 mg/l P-PO4.

As seen in the preparation step, the pH value of bio-acidification was a key parameter to maximize the release of phosphorus. Figure 3.3.9 focuses on the link between pH and Phosphorus release.

The dissolution of phosphorus was greater when the pH was lower than 4 units. Large variations are visible between the results obtained on site and those externalized. It is assumed that it is possible to achieve a dissolution of at least 60 % for a dose of co-substrate of about 2 g/g VS.

Currently, we do not have an explanation for the value obtained in test 6 which was lower than the others. On the other hand, the last trial reached performance close to

100 % of P release which is stoichiometrically not possible. Thus, the range of values to be retained as the potential of release of phosphorus is comprised between 40 and 60 %.

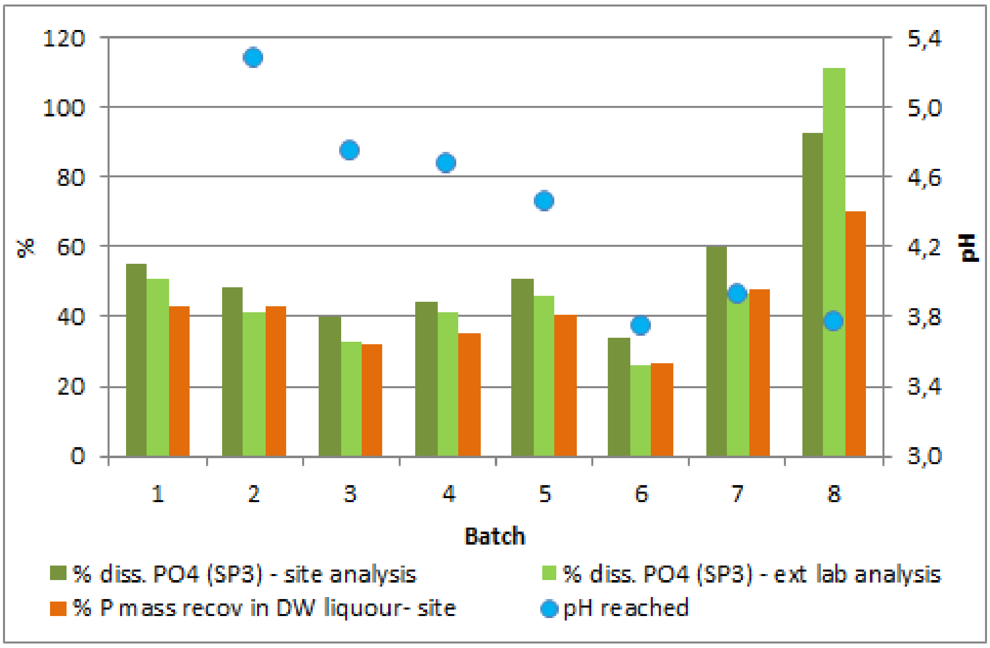


Figure 3.3.10: Percentage of solubilisation of phosphorus (left axis) and final pH (right axis) on Lille demonstrator.

An evaluation of the possible crystals from the bio-acidification centrates was made (Figure 3.3.11).

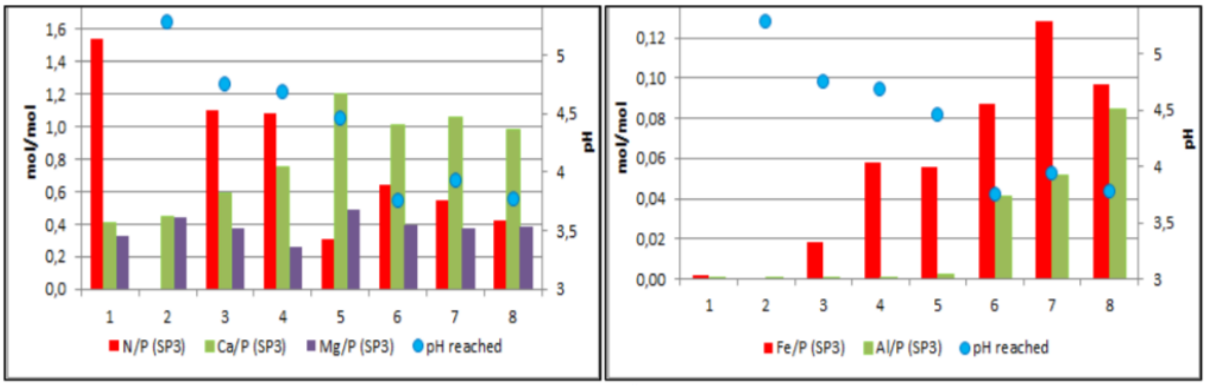


Figure 3.3.11: Mineral and metals to phosphorus ratios (molar).

When the pH dropped below 4, the Ca/P ratio was greater than the others. The crystallisation of DCP would then be favoured over that of struvite. The N/P and Mg/P ratios were close. The stoichiometry was therefore that required for the crystallisation of struvite. It was probable that the crystals produced were a mixture of both types. It is observed that the Fe/P and Al/P ratios were low (less than 0.10 mol/mol). It was therefore unlikely that phosphate would complex with either of these two elements.

Unfortunately, no start of the precipitation step was possible in Lille. Thus, the demonstrator was transferred to the Tergnier WWTP.

Tergnier upscale

Its objectives were to:

- Replicate performance obtained in Lille;
- Produce the most valuable P product (struvite or DCP or hydroxyapatite).

Successive batch of bio-acidification confirmed that a pH below 4 was necessary to maximize the release of P (Figure 3.3.9).

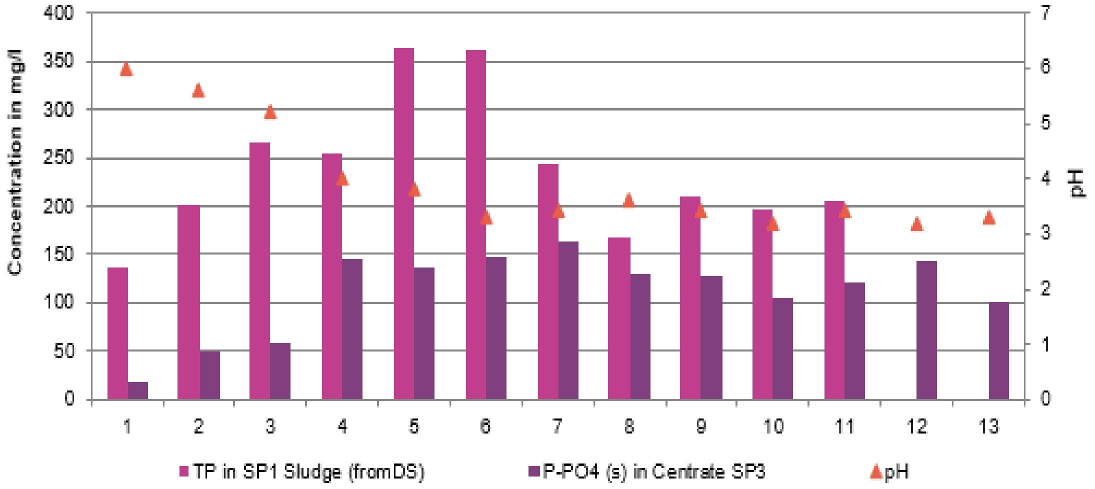


Figure 3.3.12: Phosphorus concentration (total and dissolved) on Tergnier demonstrator after bio-acidification.

Up to 150 mg/L P-PO4 is achieved with a release of 45-58 %.

Iron and Calcium are the two main cations co-released with phosphorus (Figure 3.3.13).

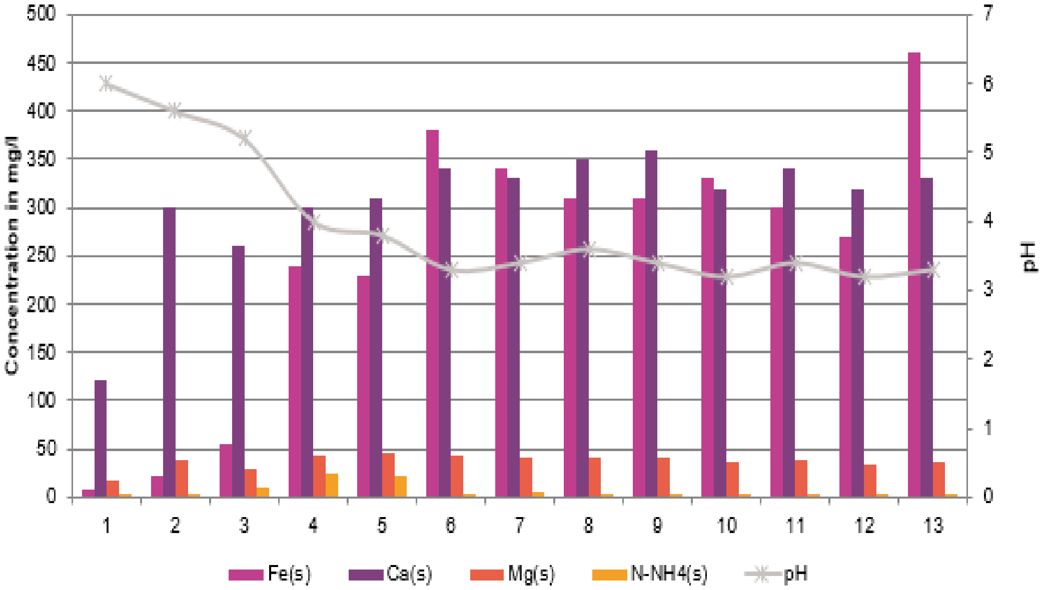


Figure 3.3.13: Dissolved minerals and cations on Tergnier demonstrator after bio-acidification.

The proper functioning of the phosphorus precipitation step is illustrated by the quality of the STRUVIA™ discharge with 4.11 mg/l at the outlet, i.e. nearly 97 % of the phosphates were captured (Table 3.3.14).

Table 3.3.14: IN/OUT balance of the STRUVIA™ process.

P-PO4 in	mg/L	120.08	
P-PO4 out	mg/L	4.11	
TSS in	mg/L	212.38	
TSS out	mg/L	207.50	
Fe in	mg/L	294.00	
Fe out	mg/L	14.32	
Dryness	%	13.70	Tergnier
Dryness	%	15.45	Lille

The best compromise of the precipitates formed was also looked after.

First, the precipitation was made in the form of struvite. It turned out to be too expensive and faced nitrogen deficiencies (NH_4^+). A second option was then the precipitation in the form of Dicalcium Phosphate (DCP) via the addition of lime. This solution turned out to be not very functional and too expensive compared to the value of the product. Finally, the production of precipitates in the form of hydroxyapatite (HAP) was made. That P product is favoured although it has no economic value but its cost of production is very low.

Figure 3.3.14 presents the precipitate of phosphorus obtained after the washing step.

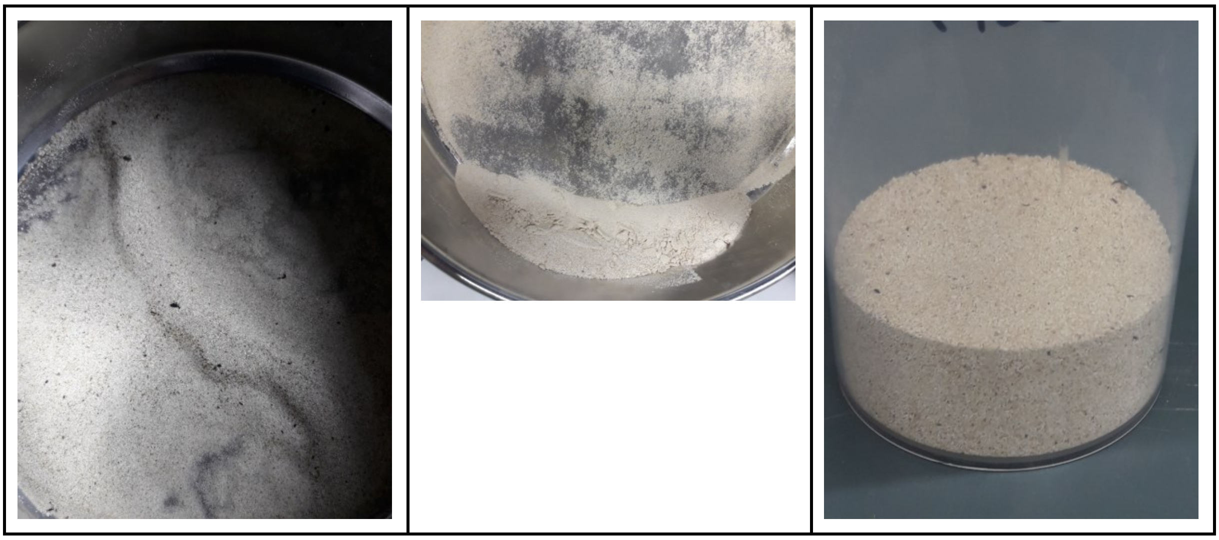


Figure 3.3.14: P-product crystals after washing (©Veolia)

3.3.3.1 *LCA for I6.1*

The Struvia™ process has been included in the LCA-LCC works done within Phos4You (cf. chapter 5).

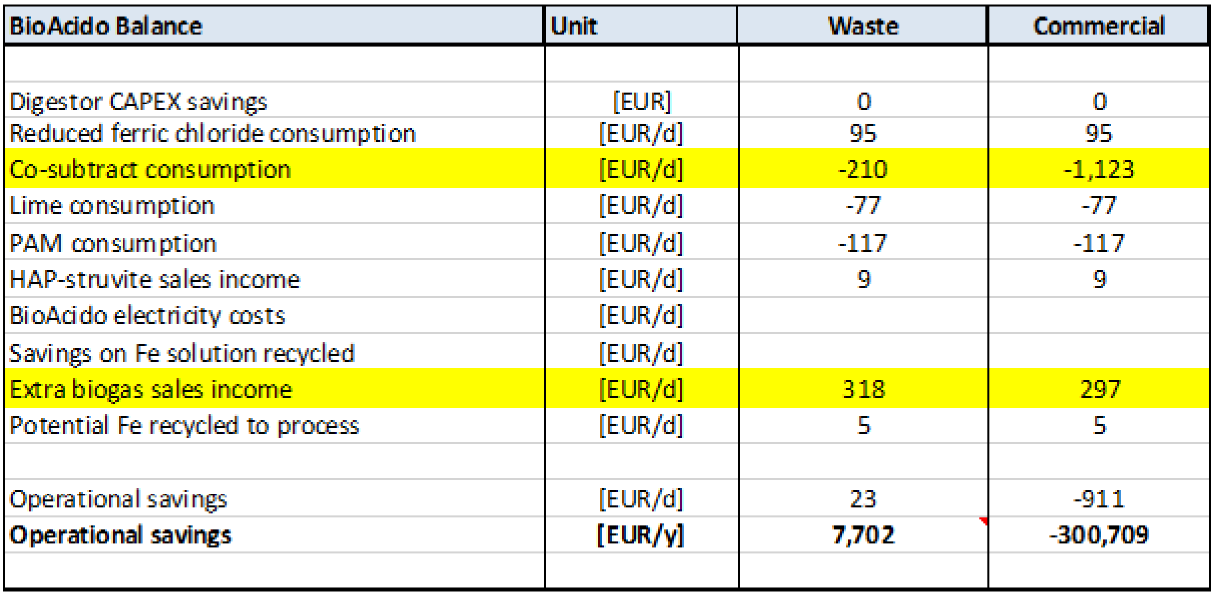
3.3.4 Discussion of results for I6.1 operation

In response of the initial 3 objectives:

- Measure the efficiency of the release of phosphorus of biological sludge resulting from a treatment of P made at least at 50 % by co-precipitation.":
  the dose of co-substrate and the maximum pH have been defined. The range of percent solubilisation of phosphorus and other ions is known.
- Confirm the effectiveness of the post-treatment (reduction of residual metals) with upscale:
  the co-release of metals and the possibilities of them polluting the final product is evaluated as very low.
- Produce the most profitable P product (struvite or DCP or HAP):
  the economic assessment concluded that the least expensive formulation of P is in the form of HAP.

In addition, the economic balance highlights three subjects. Firstly, an acceptable product is more expected than a technical product whose production cost is too high. Secondly, access to a low-cost co-substrate (preferably a waste co-substrate) is necessary so as not to reduce the revenue linked to the surplus production of biogas. Thirdly, the recovery of iron for recycling on the station requires an extraction / purification process that is too expensive compared to a purchase of the reagent (Table 3.3.15). The projection is made for WWTP of an 80 to 120 KPE.

Table 3.3.15: Economic balance.



BioAcido Balance	**Unit**	**Waste**	**Commercial**
Digestor CAPEX savings	[EUR]	0	0
Reduced ferric chloride consumption	[EUR/d]	95	95
Co-subtract consumption	[EUR/d]	-210	-1,123
Lime consumption	[EUR/d]	-77	-77
PAM consumption	[EUR/d]	-117	-117
HAP-struvite sales income	[EUR/d]	9	9
BioAcido electricity costs	[EUR/d]		
Savings on Fe solution recycled	[EUR/d]		
Extra biogas sales income	[EUR/d]	318	297
Potential Fe recycled to process	[EUR/d]	5	5
Operational savings	[EUR/d]	23	-911
Operational savings	**[EUR/y]**	**7,702**	**-300,709**

3.3.5 Conclusion for I6.1

The implementation of bio-acidification, followed by a step of precipitation of phosphorus on a larger scale was carried out. The performances of the bio-acidification step were of the same order of magnitude as those obtained at the laboratory scale by INRAE. pH and residence time conditions were confirmed. The use of agribusiness waste as a co-substrate required a slight increase in the doses to be added. The use of a low cost co-substrate (preferably a waste co-substrate) is essential so as not to reduce the income linked to the surplus production of biogas. The Struvia™ technology has proven its complementarity after the bio-acidification step with P capture yields of 97 %. The combination of both processes achieves 50 % phosphorus recovery. The modularity of Struvia™ makes it possible to produce different P products. The most valuable precipitate at this stage is HAP in terms of invest (benefit vs. chemical investment).

3.3.5.1 *Perspectives*

The conditions for the bio-acidification are close to dark fermentation. Dark fermentation is developed to produce either hydrogen or specific VFA with a high economical added value. To see if a synergy could be found between P recovery and those promising valorisation ways for sewage sludge, new experiments were performed at labscale. The main differences between bio-acidification and dark fermentation is the pH, around 4 and 5, respectively. Two semi-continuous pilots were used to tests the two processes on two different sludge, one coming from Tergnier and the other one from a large city using EBPR and Iron P removal. P dissolution was lower with dark fermentation but depending on the context and on the recycling goals, it could be interesting to think about combination of P recovery and dark fermentation. The results of these experiments have been published in 2020 in Environmental Technology (Bareha et al. 2020). Experiments and main results are summarized in Figure 3.3.15.

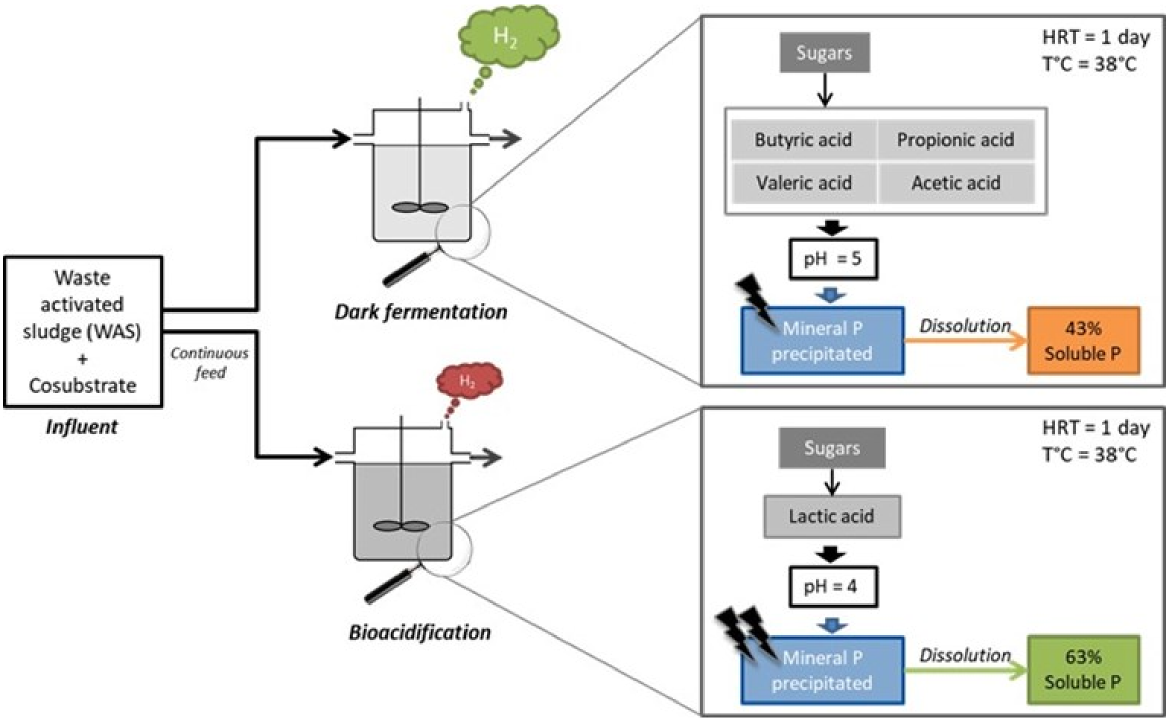


Figure 3.3.15: Comparison between dark fermentation and bio-acidification on P dissolution and VFA production

In order to predict the P dissolution, the composition of the liquid phase and therefore the quality of the solid and the amount of reactant to add for the crystallisation step, depending on the sludge characteristics and on the co-substrates available, a modelling approach was initiated. The anaerobic digestion model from the international water association (ADM1) was modified to be able to simulate the lactic acid production. However the pH is not well simulated by this model because the chemical equilibrium are not taken into account. So an algorithm was developed to combine ADM1 with the PHREEQC model developed by the USGS for simulating chemical equilibrium to be able to better simulate the pH. The combination of the two models was tested on the results of the semi-continuous experiments of bio-acidification followed by dark fermentation and give promising results for pH simulation, P dissolution and VFA production during the bio-acidification and the dark fermentation step as shown on Figure 3.3.16. Those results are to be published in 2021.

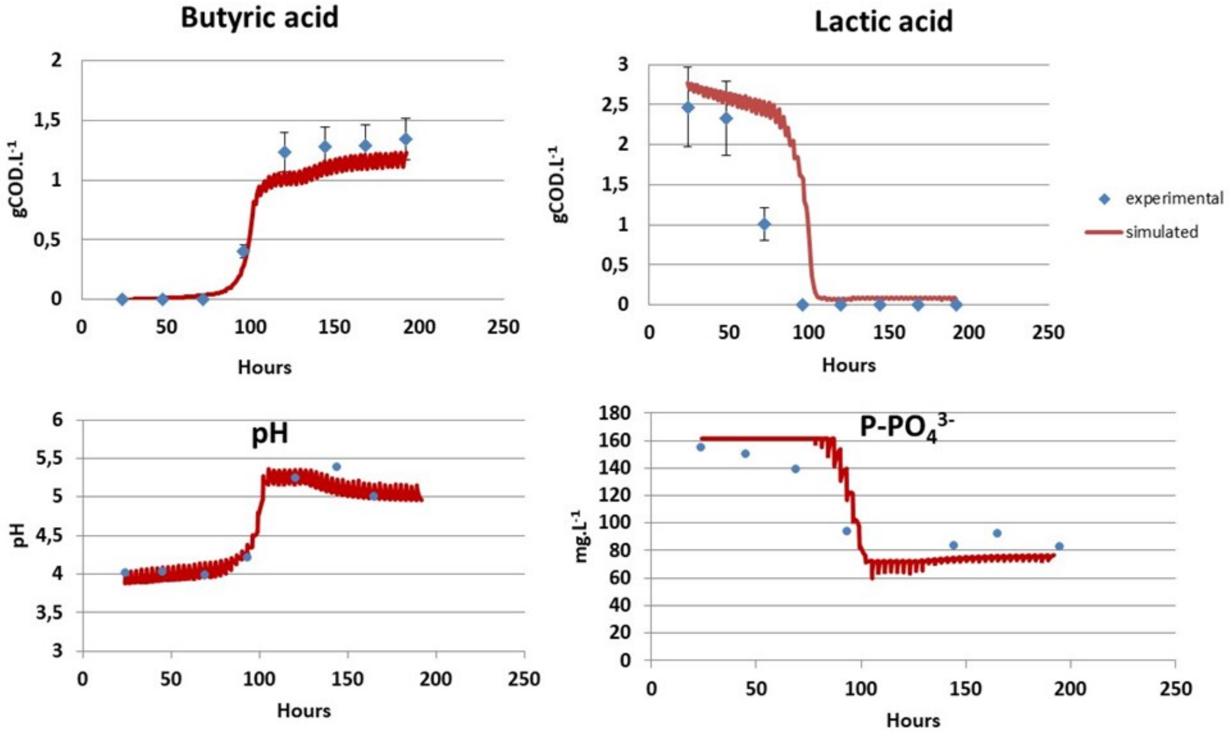


Figure 3.3.16: Comparison between experimental and simulated data during semi-continuous bio-acidification/dark fermentation experiments on Tergnier sludge (to be published)

This new modelling approach should have been tested on other sludge/co-substrates combination in order to be definitely validated.

3.4 Demonstrator I3: Acid leaching of P from partially/fully dried sewage sludge (PULSE)

Authors: Zaheer Shariff, David Leleu, Andreas Pfennig, Angélique Léonard (ULiège)

The I3 demonstrator is commissioned by ULiège in order to demonstrate the PULSE (Phosphorus University of Liège Sludge extraction) process in which P is recovered from dried sewage sludge as calcium or magnesium phosphate.

3.4.1 Preparation of I3

3.4.1.1 *PULSE process concept*

The concept of the PULSE process was developed based on the PASCH process (Doetsch et al. 2010) and further adapted to treat dried sewage sludge to recover P. The scheme of the PULSE process developed at ULiège is depicted in Figure 3.4.1. The process shown produces calcium phosphate but can also be adapted to magnesium phosphate as final product.

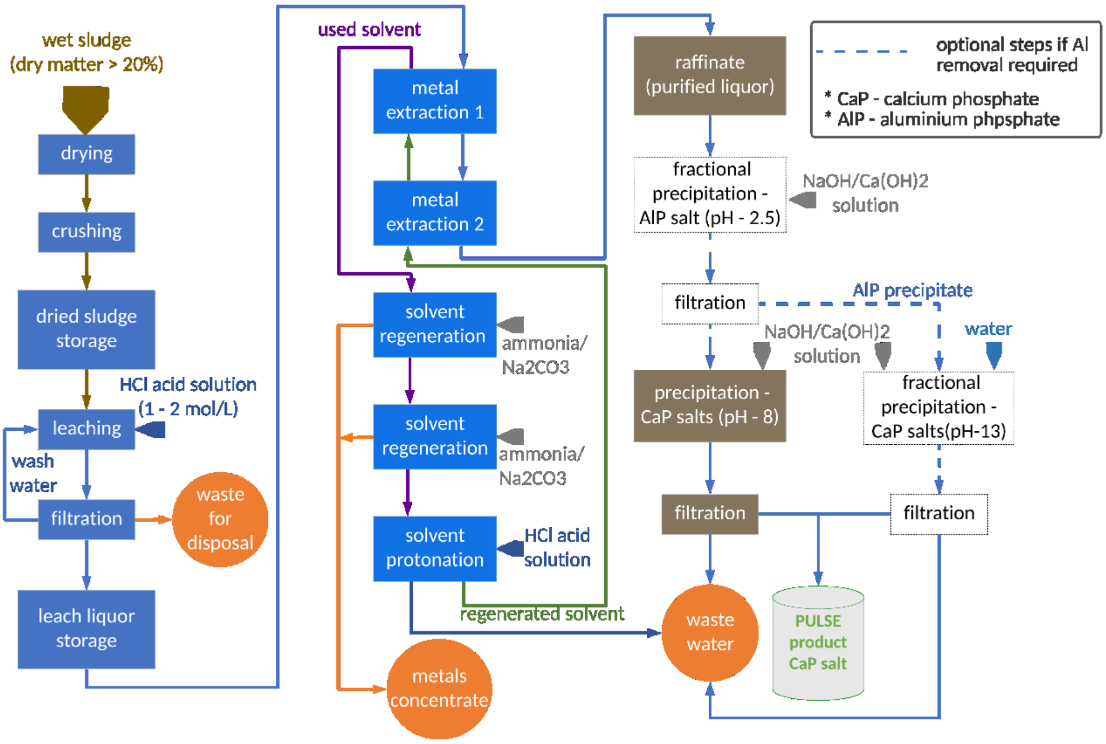


Figure 3.4.1: PULSE-process scheme.

The design and dimensioning of the I3 demonstrator was carried out based on results of laboratory experiments that were established at ULiège and information from the PASCH process as well. While the equipment and parts for the I3 demonstrator were ordered and procured, the optimisation and evaluation of individual unit operations of the PULSE process was carried out at laboratory scale by making use of the cascaded option trees and equilibrium-speciation simulations. In order to carry out the equilibrium simulations for the unit operations of the PULSE process a MATLAB tool has been developed for calculation of solid-liquid-liquid equilibria (SLLE).

3.4.1.2 *Tools used for PULSE process development and optimisation*

Cascaded option-tree evaluation

In order to find suitable operating options and to optimise the unit operations of the PULSE process, the cascaded option-tree methodology (Bednarz et al. 2014) was used. In this method, the options are evaluated against a set of operation relevant criteria. The option with the most positive evaluation is chosen for the process. The information for evaluation of the options is obtained from literature, laboratory experiments, and SLLE modelling.

Example of the cascaded option-tree evaluation to characterise the best state of the input sludge entering the PULSE process is shown in Figure 3.4.2. Dried sludge was selected as the input material for the PULSE process, because only that allowed sufficient filterability under expected process conditions.

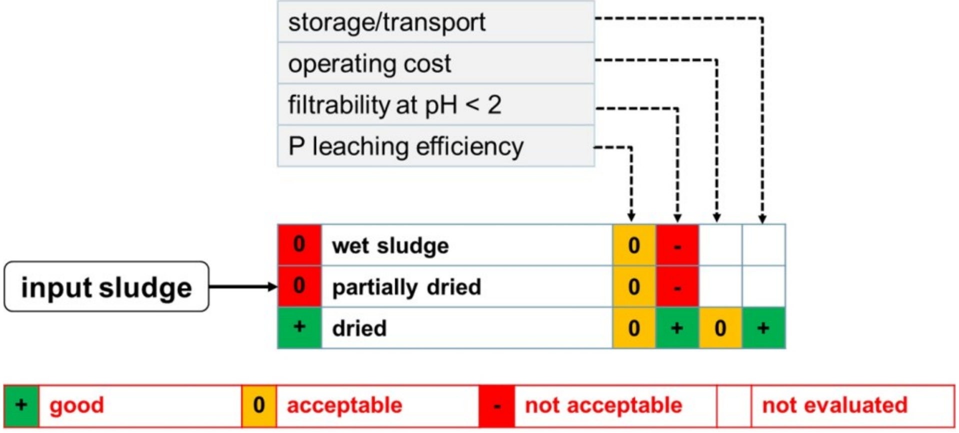


Figure 3.4.2: Cascaded option tree for sludge-input options

Similarly, different options for all unit operations of the PULSE process were analysed to identify the most suitable combination of options to be employed in the PULSE process, some of which are presented in the following sections.

Solid Liquid Liquid equilibrium modelling tool

The chemical unit operations of the PULSE process, i.e. leaching, solvent extraction of metals and subsequent stripping of metals from the spent solvent for regeneration, and the precipitation of P salts are inter-dependent and sensitive to the pH of the respective operation among other operating parameters. As the characteristics of sludge can vary from day to day, it is imperative to understand the chemistry and reactions occurring as a function of pH in each of these operations. Therefore, a MATLAB tool for simulating SLLE was developed, which can be used to describe the chemical unit operations. With the help of this tool, it is possible to optimise the process for sludge with different characteristics minimizing experimental work.

The SLLE tool solves a set of nonlinear equations consisting of charge neutrality, mass balance and law of mass action constraints which describe the system (Shariff et al. 2020), including appropriate quantification of thermodynamic non-idealities. The solution of the non-linear system of equations leads to the concentrations of all chemical species that exist in the aqueous phase and/or in the organic phase as well as the solids that can precipitate at equilibrium as shown in Figure 3.4.3. In that example, representing undigested dewatered sludge used for performing experiments to develop the PULSE process contained calcium, iron and aluminium as the pre-dominant metals besides phosphorus. Analysis of Ferric and ferrous iron leached from the dried sludge revealed that about 70 % of the iron were present as Ferric, Fe^{3+}. Depending on the molar concentration of iron, a major fraction of inorganic phosphorus in sludge can be present as ferric phosphate ($FePO_4$). It can be seen from Figure 3.4.3, $FePO_4$ can remain undissolved if the pH is greater than 0.3.

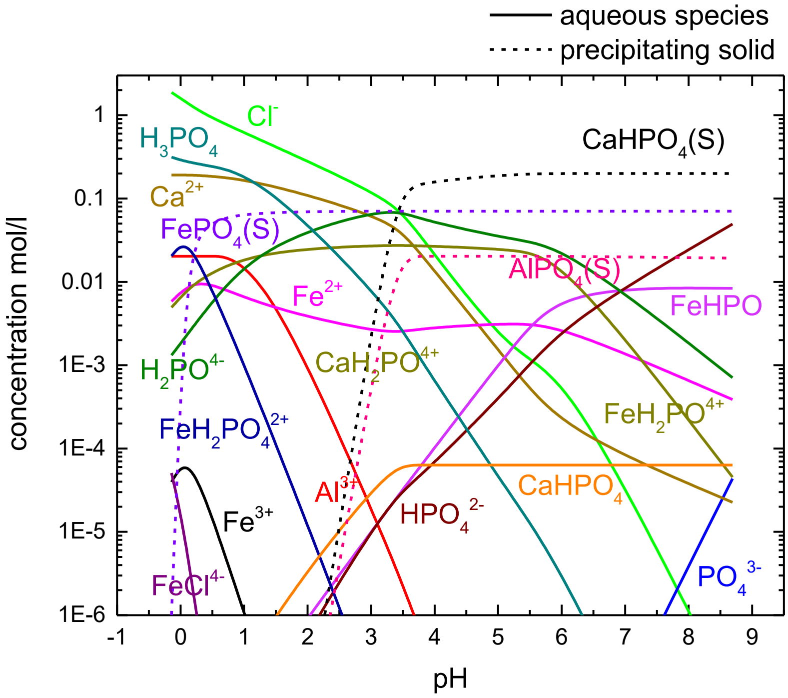


Figure 3.4.3: Speciation using the SLLE tool. Initial concentrations in [mol/L]: Fe3+: 0.0703, Al3+: 0.0203, HCl: varying, PO4-3: 0.348, Ca2+: 0.2, Fe2+ - 0.03. The dashed curves show the precipitation equilibrium

The SLLE tool allows simulations both by fixing the input amounts for the components to obtain the equilibrium concentrations and pH, or alternatively to calculate the amount of pre-defined component needed to reach a desired pH. It is also possible to calculate the equilibrium concentration of different species when two solutions containing different components are mixed.

The input data to the SLLE tool includes the total input amount or concentration of the different components, the chemical equilibrium constants and the reaction stoichiometry. With this input information, the SLLE tool determines the output concentrations of the aqueous species and the amount of solids that precipitate depending on the equilibrium conditions for each step of the PULSE process.

Although extensive thermodynamic data are available for aqueous phase reactions and precipitation, it is not the case for solvent extraction or organic phase reactions. Since the description of these equilibria is required to optimise the PULSE process, the chemical equilibrium constants and reaction stoichiometry are determined in this case by performing equilibrium experiments and fitting the parameters to experimental data using the tool.

3.4.1.3 *PULSE-process development and optimisation with lab experiments*

Lab-scale experiments for each unit operation of the PULSE process were established in order to obtain the necessary information for the design of the I3 demonstrator and to develop and optimise the overall process. The general outcomes of the process development and optimisation for the individual unit operations of the PULSE process are discussed below. All the laboratory experiments were carried out using undigested dewatered sludge from Oupeye wastewater treatment plant (WWTP) in Liège, Belgium.

Sludge drying

The P-leaching efficiency of dried sludge (DS) and dewatered sludge (DWS) was compared after leaching with hydrochloric acid (HCl) in order to select the optimal input material to the process. A batch convective air dryer was used for drying the sludge. The drier also allows for the continuous monitoring of the weight of sample. The sludge was dried at 110 - 120°C until no further change in the weight of the sludge sample was observed. After drying, the sludge was crushed to a particle size of <5 mm and stored. The dry matter content was measured just before leaching and it was found to be 98.2 %. The dried sludge was leached using a solid-liquid ratio by weight of 0.25 i.e. 250 g of dried sludge was mixed with 1 litre of HCl solution. In case of dewatered sludge, which has a paste-like appearance as shown in Figure 3.4.4, the liquid fraction is already about 0.75. Therefore, in the latter case, excess of acid solution is required to solubilize the pasty sludge and to overcome the dilution effect due to the water content of the sludge itself. Laboratory tests indicated that at least twice the amount of water or acid solution must be added to the dewatered sludge to convert it to fluid form. The equilibrium pH of the liquor after leaching and separation of solids was 0.4 and 0.5 for dried sludge and dewatered sludge, and the leaching efficiency was found to be 69.1 % and 72.6 %, respectively. This indicated that drying of sludge had negligible influence on the P-leaching efficiency but reduced the amount of acid required to reach the desired pH.

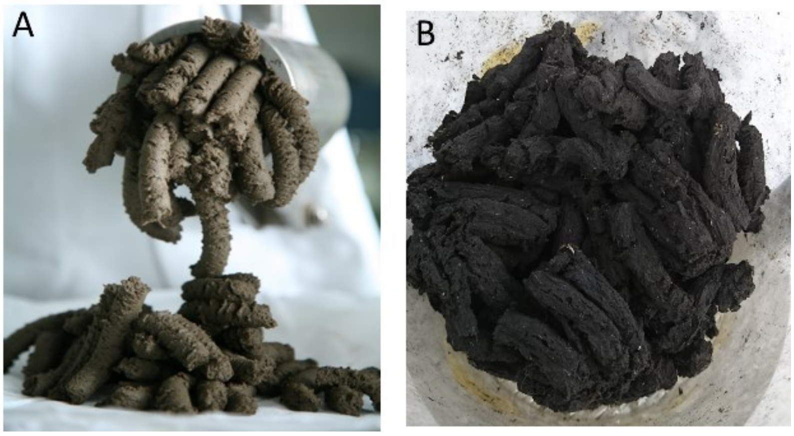


Figure 3.4.4: Texture of undigested dewatered sludge from Oupeye WWTP (A): 20 to 22 %DM & dried sludge (B): >97 %DM

A simple cost comparison for the typical energy requirement to dry 1 kg of dewatered sludge and the excess amount of acid that must be used for the subsequent leaching at pH < 1 was worked out. It was evaluated that the cost for drying the sludge using the currently available technologies was almost the identical or only slightly above the cost of the excess acid that must be used to leach the dewatered sludge. Further, with respect to solid-liquid separation after the leaching operation, in the case of dewatered sludge it was not possible to filter out the solids at 100 or 50 µm as the solids were very fine and the use of a finer filter blocked the filter almost immediately. In contrast, for dried sludge the particle size could be controlled to a certain degree by the crushing intensity and hence removal of more than 80 % particles at 100 or 50 µm was possible by filtration. These results are indicated in Figure 3.4.2 above.

Considering the reduction in acid consumption during leaching and the ease of solid-liquid separation after leaching in case of dried sludge, a drying step was included in the PULSE process. For the I3 demonstrator a batch forced ventilation drier with a capacity of drying up to 80 kg of dewatered sludge in a single batch was selected after comparing the different options on the market in the corresponding capacity range.

Leaching

The efficiency of overall P-recovery is largely dependent on the leaching operation. Various options and operating parameters were tested in order to evaluate the leaching of P from dried sludge such as leaching acid, pH, time, temperature and effect of addition of oxidizing and reducing agents during leaching. All the leaching experiments were conducted at room temperature if not otherwise indicated. Typically, sludge was dried and stored in air tight containers and the DM was measured each time before leaching. No differences could be observed in leach liquor of dried sludge stored even for more than 6 months.

It can be seen from Figure 3.4.5 that the leaching of P depends only on the pH and not on the acid used. It is also realised that the maximum leaching efficiency that could be reached even at a very low pH of -0.16 is about 65 %.

The P in sludge used for leaching experiments was characterised using the Standards, Measurements and Testing (SMT) harmonized procedure for phosphorus fractionation in freshwater sediments (SMT protocol). The sludge from the Oupeye WWTP was found to contain about 68 % inorganic P, while 32 % of P were bound to organic solids. This means, the P leached in acidic conditions is largely stemming from the inorganic P while little or no organic P can be accessed around pH zero. The leaching of P estimated using the SLLE tool is also shown in Figure 3.4.5, which correlates well with the experimental data. Thus, if the major inorganic components of the sludge are known, the leaching efficiency can be evaluated using the SLLE tool as a function of pH.

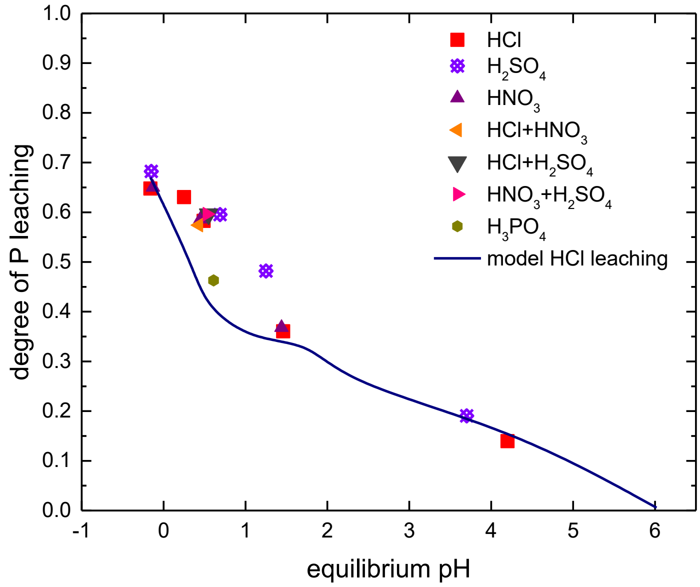


Figure 3.4.5: P-leaching efficiency from DS. Sludge: Oupeye WWTP, S/L ratio: 0.25, leaching duration: 60 min, DM: >97 %, room temperature

The use of hydrogen peroxide as oxidizing agent or sodium sulfite as reducing agent had no influence on the P-leaching efficiency. Also, the increase in temperature up to 35°C did not have any measurable effect. The P leaching was almost completed in one hour as shown in the Figure 3.4.6 and the solid-to-liquid ratio at values less than 0.25 did not have any influence on P leaching either.

Drying of sludge under conditions indicated that the drying time and drying technique may have an effect on the leaching. Three different drying procedures were compared, i.e. connective air drying which is comparatively faster, drying at 80 to 100 °C without any air circulation, which is slow, and drying in an oven at 105 °C. In all the cases, the sludge was dried until the DM content was >97 %, but the duration of drying differed due to the temperature and the drying conditions, and also because the different dryers could accommodate different amounts of sample. As shown in the Figure 3.4.7, the sludge by convective air drying has the lowest P, iron and organic carbon leaching as compared to the sludge which was dried for longer duration with no air circulation. The initial impression is that, due to the longer drying times in that latter, there could be break down of organic matter which results in the increased leaching efficiencies.

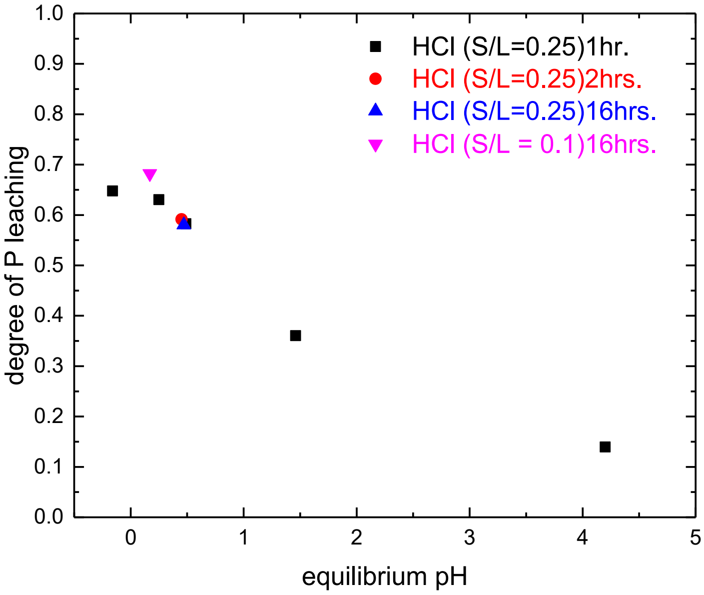


Figure 3.4.6: Effect of leaching time and S/L (solid-to-liquid) ratio on P leaching efficiency. Sludge: Oupeye WWTP, DM: >97 %

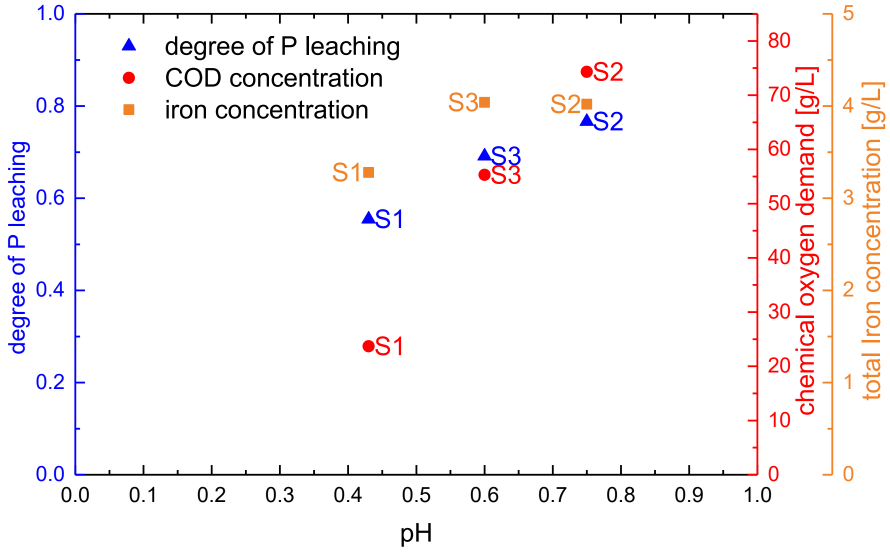
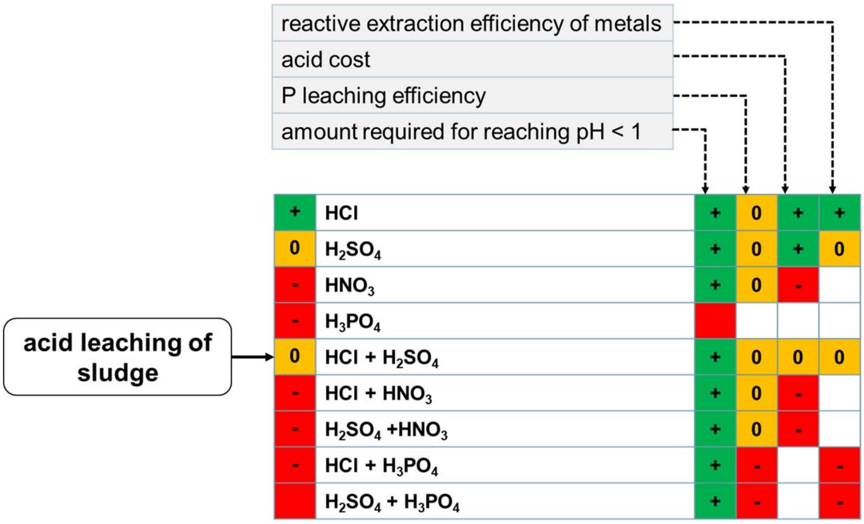


Figure 3.4.7: Effect of drying mechanism on leaching of sludge. Sludge: Oupeye WWTP, DM: >97 %, S1 – - rapid convective air drying for 4 h, S2 – slow drying without air circulation for 72 h at 80 to100 °C, S3 – drying without air circulation for 24 h at 100 °C

With respect to the different acids tested for leaching, HCl is one of the cheapest acids and it also provided better result with respect to solvent extraction of metals in comparison to sulfuric acid. Therefore, based on the cascaded option-tree evaluation of the different acids as shown in Figure 3.4.8, it was decided to use HCl in the PULSE process. Further, based on the laboratory results, leaching of 1 hour and an S/L ratio of 0.25 were chosen for the PULSE leaching. Further increase in S/L ratio may lead to operational difficulties due to the increase in percentage of solids in the liquor, and a decrease in S/L did not have any advantage, rather it would increase the volume of liquor that would have to be treated in the downstream steps.



		amount required for reaching pH < 1	P leaching efficiency	acid cost	reactive extraction efficiency of metals
+	HCl	+	0	+	+
0	H_2SO_4	+	0	+	0
-	HNO_3	+	0	-	
-	H_3PO_4	🟥			
0	HCl + H_2SO_4	+	0	0	0
-	HCl + HNO_3	+	0	-	
-	H_2SO_4 +HNO_3	+	0	-	
-	HCl + H_3PO_4	+	-		-
🟥	H_2SO_4 + H_3PO_4	+	-		-

Figure 3.4.8: Cascaded option-tree evaluation of the acid to be used for sludge leaching

For the I3 demonstrator dimensioning, if 100 kg of dewatered sludge are to be treated per batch, considering a DM content of 20 % will yield 20 kg of dried sludge. If the leaching is performed at S/L ratio of 0.25, 100 l of acid solution will be required for each batch. Therefore, the leaching tanks were dimensioned by considering the above flowrates for sludge and acid and a leaching time of 1 h.

Reactive extraction

The metals that are co-leached with P are not desired in the final product as they may be detrimental when the recovered P product is used as a fertiliser or they may reduce the P availability to plants. For example, the metals that are leached from sludge along with P are shown in Figure 3.4.9.

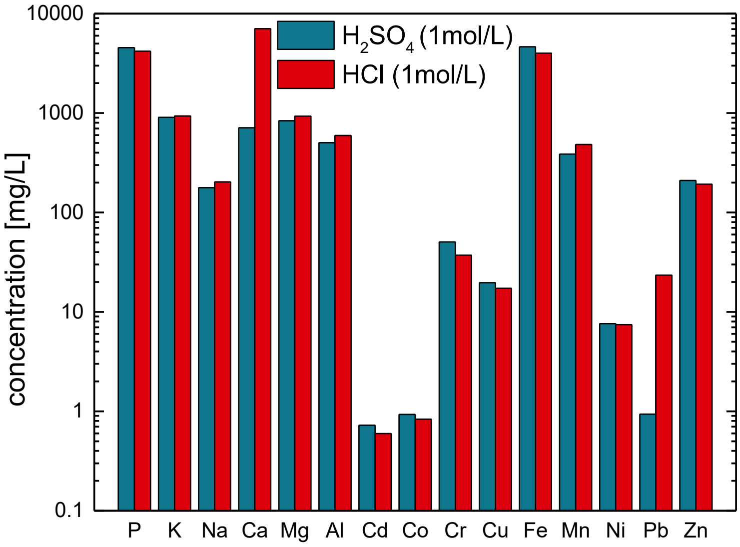


Figure 3.4.9: Nutrients and metals leached from sludge with H_2SO_4 and HCl. Sludge: Oupeye WWTP, DM: >97 %, S/L: 0.25, leaching duration: 1 h

Apart from P and Ca, Fe is the most predominant metal leached from Oupeye sludge and 70 % of Fe is present in the form of Fe^{3+} as analysed in the leach liquor. It has been already indicated that $FePO_4$ can precipitate even at a pH as low as 0.3, which would reduce the P availability to plants in the soil.

In the PULSE process, reactive solvent extraction is used to remove Fe and other heavy metals from the leach liquor. Reactive extraction allows the selective extraction of metals as a function of pH and has a high capacity for metal loading. Based on the information obtained from the PASCH process and the mechanism of extraction, three extractants were evaluated, namely Alamine 336, which is an anion-exchange extractant, D2EHPA, which represents a cation-exchange extractant, and TBP, which is a complexing extractant. Ketrul-D80 which is a commercially available brand of desulfurized kerosene was chosen as diluent. Kerosene is one of the most commonly used diluents due to the advantages it offers over other diluents such as low toxicity and high flash point. The extraction efficiencies of these extractants were evaluated using lab experiments for both H_2SO_4 and HCl based leach liquors at 1 mol/L concentration. In case of H_2SO_4 based leach liquor, the extraction efficiency for the metals analysed was below 20 %. Therefore, it was decided not to use H_2SO_4 for leaching in the PULSE process. The extraction efficiency of metals with HCl is shown in Figure 3.4.10.

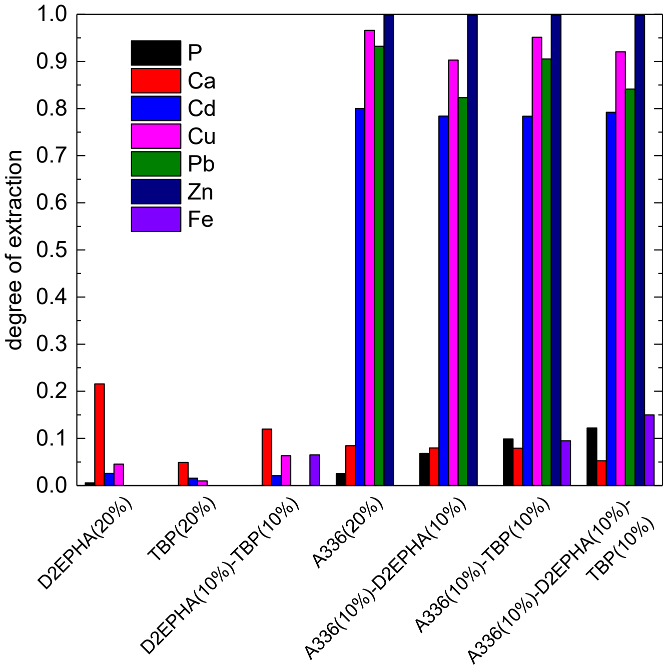
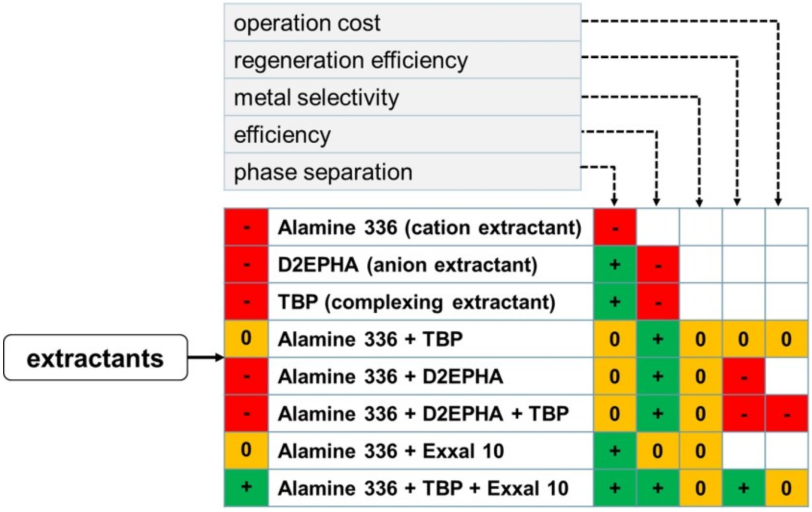


Figure 3.4.10: Extraction efficiency of metal from HCl at1 mol/L based leach liquor, diluent: Ketrul-D80, modifier for Alamine336: Exxal10, solvent concentration indicated in vol %, O/A phase ratio: 2

Experimental results indicated that only the reactive extractant Alamine 336 provided a quantitative extraction of metals. The degree of extraction of Iron as indicated in Figure 3.4.10 is very low at a HCl concentration of 1 mol/L. It was found to increase with the concentration of HCl, as Cl^- is exchanged against negatively charged ferric-chloride complexes that are formed at low pH. Also, with regards to Fe, only anionic complexes of ferric were extracted and, therefore, any ferrous ions in the leach liquor have to be oxidized to Ferric before extraction. It was determined that a dosage of hydrogen peroxide (50 % concentrated) of 2 ml/L leach liquor was sufficient to oxidize the ferrous to ferric and improve the extraction efficiency.

Based on the cascaded option tree evaluation as shown in Figure 3.4.11, the solvent system containing Alamine 336, TBP and Exxal 10 dissolved in Ketrul D80 was chosen to be employed in the PULSE process. Exxal 10 is a modifier that is required to improve the solubility of Alamine 336 in the diluent and to prevent the formation of a third phase upon extraction. Typically, Exxal 10 equivalent to about 50 % of the volume fraction of Alamine 336 must be added to avoid that third-phase formation. However, it was found that Exxal 10 may lead to a decrease in the extraction efficiency. Therefore, Exxal 10 was supplemented by TBP, which also acts as a modifier and contributes to a slight increase in the extraction efficiency. A protonation step is required for Alamine 336 before the actual extraction, during which it is loaded with anions such as Cl⁻ which undergo the exchange reaction during extraction of the anionic metal species.



	extractants	phase separation	efficiency	metal selectivity	regeneration efficiency	operation cost
-	**Alamine 336 (cation extractant)**	-				
-	**D2EPHA (anion extractant)**	+	-			
-	**TBP (complexing extractant)**	+	-			
0	**Alamine 336 + TBP**	0	+	0	0	0
-	**Alamine 336 + D2EPHA**	0	+	0	-	
-	**Alamine 336 + D2EPHA + TBP**	0	+	0	-	-
0	**Alamine 336 + Exxal 10**	+	0	0		
+	**Alamine 336 + TBP + Exxal 10**	+	+	0	+	0

Figure 3.4.11: Cascaded option tree for the selection of extractants

Multiple experiments were performed for certain concentrations of the extractants in order to check the repeatability. The results obtained with multiple tests had a deviation of less than 10%.

For the purpose of process optimisation, extraction-equilibrium experiments were performed in the laboratory and the results were used to fit the extraction equilibrium and stoichiometry using the SLLE tool as these data are not available in literature. The fitted thermodynamic data are then used in the SLLE tool for optimisation of the extraction operation. The equilibrium experiments were performed by varying the different components of the system, i.e. concentration of extractant and HCl.

For example, the extraction of iron by Alamine 336 + TBP can generally be written as

$$FeCl_m^{3-m} + \overline{n(R_3NTBPHCl)} \rightarrow \overline{FeCl_m(R_3NTBPH)_n} + nCl^- \tag{3.1}$$

The equilibrium extraction constant is then given by the law of mass action as

$$K_{ext} = \frac{\overline{\left[FeCl_m(R_3NTBPH)_n\right]}\,[Cl^-]^n}{\left[FeCl_m^{3-m}\right]\overline{[R_3NTBPHCl]}^n} \tag{3.2}$$

The equilibrium extraction constant K and the stoichiometry of extractant with respect to Fe, are obtained by fitting the experimental data using the SLLE tool. The results of fitting are shown in the Figure 3.4.12.

Since the stoichiometric coefficient n is not an integer, this indicates that there may be two different Fe^{3+} complexes that are being extracted and n and K are the averages for the two complexes, i.e.

$$FeCl_4^- + \overline{(R_3NTBPHCl)} \rightarrow \overline{FeCl_4R_3NTBPH} + Cl^- \tag{3.3}$$

$$FeCl_5^{2-} + \overline{2(R_3NTBPHCl)} \rightarrow \overline{FeCl_5(R_3NTBPH)_2} + 2Cl^- \tag{3.4}$$

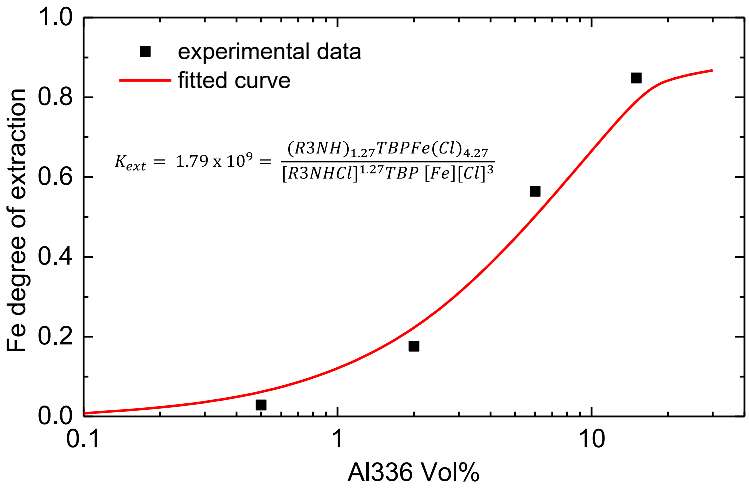


Figure 3.4.12: Fitting of extraction constant log *K_{ext}* and stochiometric coefficient for extraction of Fe from HCl based leach liquor. Solvent: 10 vol-% Alamine 336 + 10 vol-% TBP + 3 vol-% Exxal 10 + 77 vol-% Ketrul D80 -, O/A phase ratio: 1

After extraction, the spent solvent can be regenerated and reused, which for the complex of Alamine 336 and TBP can be realised by reacting the spent solvent with an alkaline solution. Based on the information from the manufacturer of Alamine 336 and literature, different regenerating solutions were selected and evaluated. The stripping efficiency of the different regenerating solutions to strip the metals form the loaded solvent is shown in Figure 3.4.13. It can be seen that the re-extraction efficiency for the analysed metals was considerably higher when alkaline solutions were used in comparison with just water. During stripping, some of the metals precipitated as hydroxides in the aqueous phase. Further, it was noticed that during stripping the precipitation of metals made the phase separation difficult if lower concentrations of base solutions were used. Therefore, either very low concentrated stripping solutions must be used ensuring that the precipitation pH is not reached in the aqueous phase or excessive base concentration at which phase separation can be achieved despite precipitation of metals must be used.

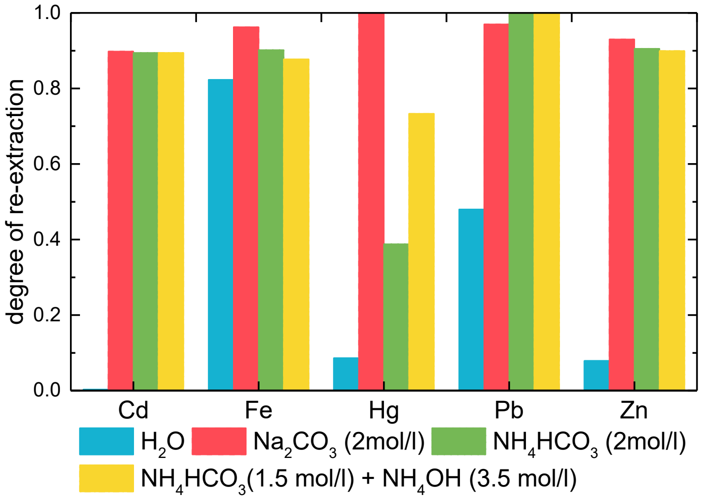


Figure 3.4.13: Degree of re-extraction of metals from spent extractant. Spent extractant; 10 vol-% Alamine 336 + 10 vol-% TBP + 3 vol-% Exxal 10 + 77 vol-% Ketrul D80, O/A phase ratio: 1

Based on the evaluation of the cascaded option tree, either sodium carbonate or a mixture of ammonia and ammonium bicarbonate can be used as the stripping agents. To further optimise the re-extraction process, equilibrium experiments of solvent stripping were carried out at different concentrations of both sodium carbonate and mixture of ammonia and ammonium hydrogen carbonate solutions. The stripping efficiency of metals at different concentration of sodium carbonate is shown in Figure 3.4.14 as an example. It can be seen that the stripping was also dependent on the pH and the metal-chlor complex formation as expected.The degree of stripping calculated by the model using the fitted parameters follows the experimental data and lies within at most 15 % deviation.

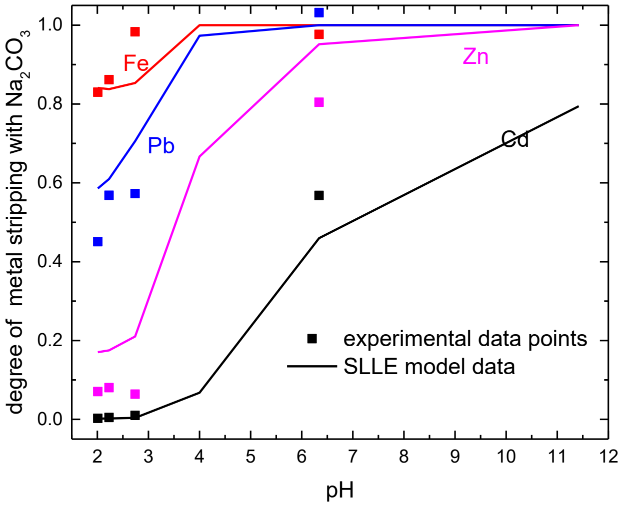


Figure 3.4.14: Degree of stripping of metals from the spent solvent at different concentrations of Na2CO3. Spent extractant; 10 vol-% Alamine 336 + 10 vol-% TBP + 3 vol-% Exxal 10 + 77 vol-% Ketrul D80, O/A phase ratio: 1

Thus, the SLLE model may be used to optimise the solvent extraction and regeneration based on the concentration of the metals in the leach liquor with less experimental effort while operating the I3 demonstrator.

To design the mixer settler equipment for the I3 demonstrator, settling experiments for the extraction step were carried out and evaluated using the ReDrop program (Leleu and Pfennig 2019). A settling time of 491.8 s and a drop diameter of 0.388 mm was estimated using the program as seen in the Figure 3.4.15.

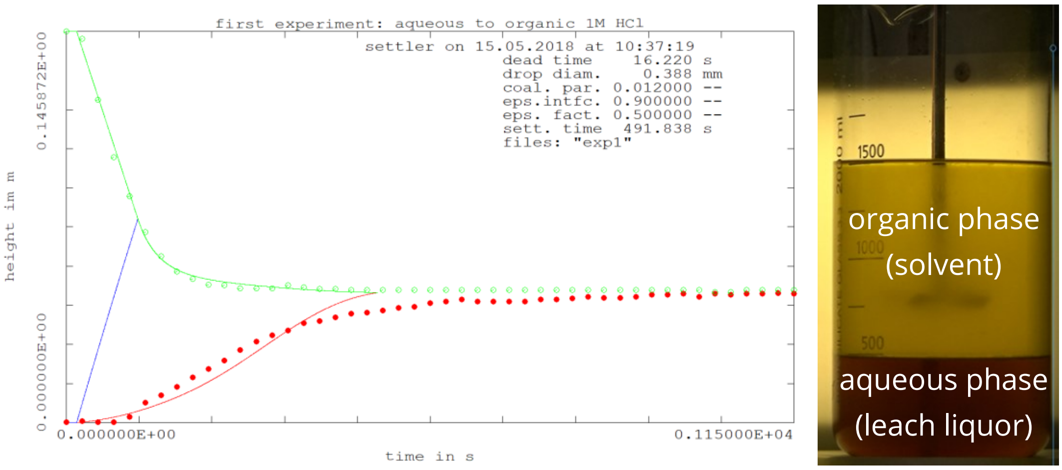
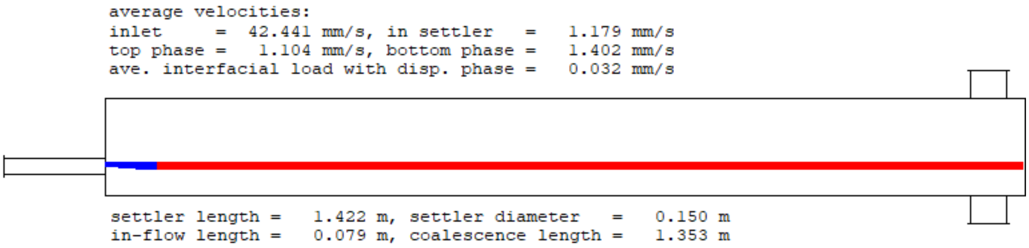


Figure 3.4.15: Evaluation of phase separation and drop diameter for separation of organic and aqueous phase. Extractant; 10 vol-% Alamine 336 + 10 vol-% TBP + 3 vol-% Exxal 10 + 77 vol-% Ketrul D80, leach liquor: 1 mol/L HCl, O/A phase ratio: 2

Based on the data obtained from the settling experiments, the size of the settler was evaluated using the settler program (Leleu and Pfennig 2019). For a total flowrate of 75 L/h at an O/A phase ratio of 2 and a settler diameter of 0.15 m, the length of the settler was evaluated to be 1.422 m as shown in Figure 3.4.16.



```
average velocities:
inlet      =  42.441 mm/s, in settler    =   1.179 mm/s
top phase =   1.104 mm/s, bottom phase =   1.402 mm/s
ave. interfacial load with disp. phase =   0.032 mm/s

settler length =   1.422 m, settler diameter    =   0.150 m
in-flow length =   0.079 m, coalescence length =   1.353 m
```

Figure 3.4.16: Estimation of settler length

A battery of four mixer settlers with the above dimensions is employed in the PULSE demonstrator to carry out the different steps involved in solvent-extraction, i.e. protonation of solvent using acid, extraction of metals in two counter-current stages and stripping of metals from solvent.

Precipitation

In the PULSE process, it is possible to precipitate P either as calcium phosphate (CaP) or as magnesium phosphate (MP). Since precipitation of MP requires and additional step for the removal of calcium as calcium sulfate by fractional precipitation, it is preferred to precipitate P as calcium phosphate. In order to evaluate the precipitation of P as a function of pH and to optimise the process, experiments were conducted with NaOH and $Ca(OH)_2$ at different pH for P precipitation. The total mixing time of the reaction mixture was twenty minutes and the temperature at the end of mixing for all the experiments was about 30 °C. The concentration of the P and other elements in the sludge leach liquor after extraction that was used for precipitation experiments is shown in Table 3.4.1.

Table 3.4.1: Concentration of components in sludge leach liquor from Oupeye sludge before and after extraction. Leaching acid conc. 2 mol/L HCl; extraction with 10 vol% Alamine 336 + 10 vol% TBP + 3vol% Exxal 10 in Ketrul D80; extraction stages: 2; O/A phase ratio: 1

component	before solvent extraction mg/L	after solvent extraction mg/L
Al	503	506
As	1.36	1.31
Ca	6330	6470
Cd	0.694	0.0005
Co	0.578	0.585
Cr	37.7	35.7
Cu	49.4	34
Fe	3340	16.4
Hg	0.0019	0.0009
K	1150	1130
Mg	1030	1040
Mn	214	206
Ni	5.69	5.62
P	4270	3810
Pb	24.92	0.939
Zn	202	< 0.3

The precipitation of different components as a function of pH using with 5 mol/L of NaOH is shown in Figure 3.4.17. The different calcium-phosphate phases that could precipitate at different pH were evaluated based on the SLLE model considering the solubility-product constant of the various calcium-phosphate phases and the Ca/P ratio that was found in the precipitate. The results of the evaluation are shown in Figure 3.4.18. The precipitation of different phases is quite complex as at first a less stable phase such as di-calcium phosphate di-hydrate ($CaHPO_4.2H_20$) or amorphous calcium phosphate ($Ca_3(PO_4)_2$) is precipitated which transforms into the more stable hydroxyapatite (HAP) ($Ca_5(PO_4)_3OH$) (Montastruc et al. 2003). The time for transformation of the precursors to HAP depends on various factors such as temperature, saturation, presence of other ions such as magnesium and carbonates.

Since aluminium (Al) is not removed during extraction an excess of aluminium in the leach liquor could be removed by fractional precipitation. As seen in the Figure 3.4.17, all the aluminium is precipitated at pH 3 as $AlPO_4$. Therefore, a fractional precipitation of Al can be carried out around pH 3. And since Al re-dissolves at pH >10, this fractional precipitate can be re-dissolved to solubilize Al while adding Ca, to recover the corresponding P.

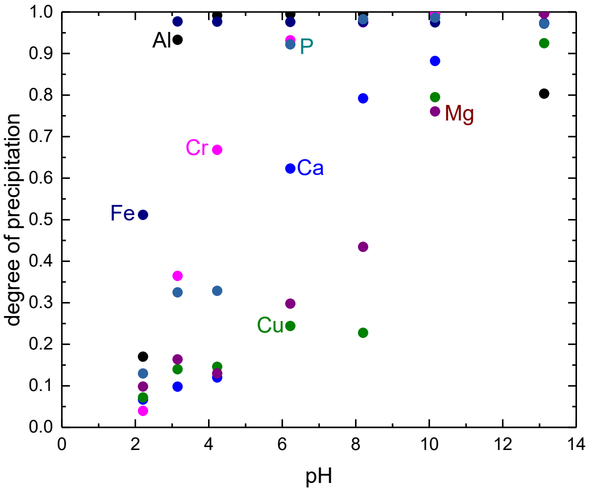
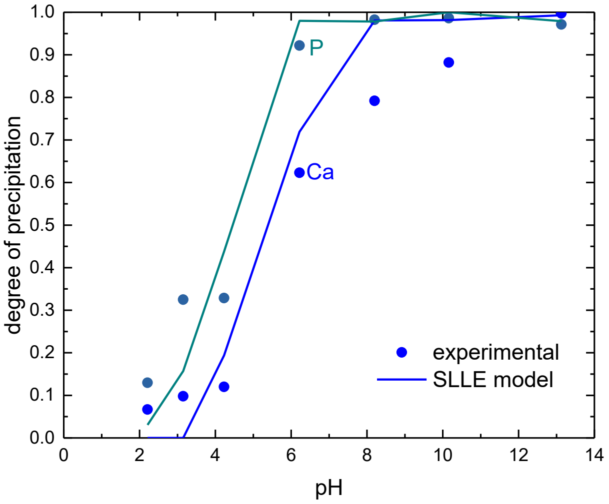


Figure 3.4.17: Precipitation of different components from extracted sludge leach liquor as a function of pH with 5 mol/L NaOH



pH	2.21	3.15	4.23	6.22	8.22	10.16	13.13
Ca/P	0.84	0.70	0.88	1.06	1.17	1.42	1.34
	no CaP precipitation		$CaHPO_4.2H_20$		amorphous $Ca_3(PO_4)_2$		$Ca_4H(PO_4)_3$ $.2.5H_2O$

Figure 3.4.18: Simulation of Ca and P precipitation using SLLE tool

During precipitation with a 25% slurry of $Ca(OH)_2$ as shown in Figure 3.4.19, about 70% of P precipitated at a pH of 4 and in comparison, only about 35% precipitated while using NaOH. This was due to the excess of Ca^{2+} which leads to the saturation for more CaP precipitation even at pH 4. Furthermore, more than 90% of P had precipitated in both the cases at pH 6.

Therefore, for the demonstrator tests, it is decided to use a pH between 5 and 6 for the precipitation. As $Ca(OH)_2$ is cheaper compared to NaOH, it is more desirable to use $Ca(OH)_2$ compared to NaOH for the precipitation.

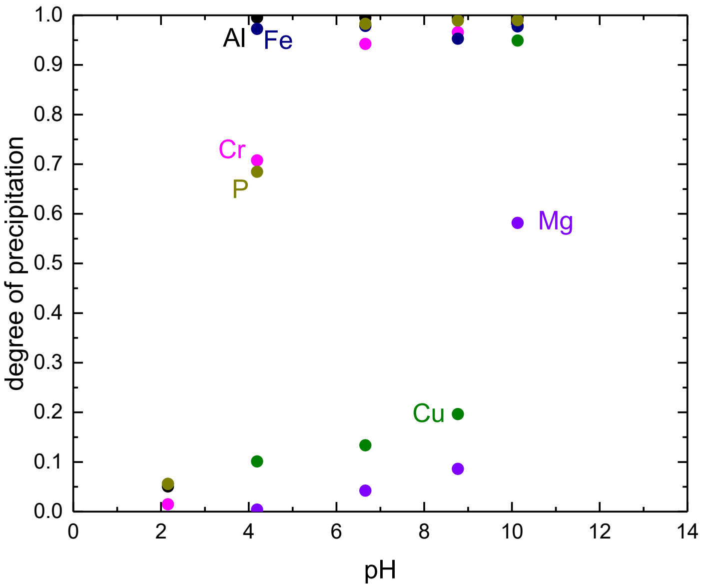


Figure 3.4.19: Precipitation of different components from extracted sludge leach liquor as a function of pH with 25% $Ca(OH)_2$ slurry in PULSE process

Solid-liquid separation

There are two solid-liquid separation steps in the PULSE process, one after the leaching operation and the second after the precipitation. At laboratory scale the solid-liquid separation after leaching was performed either by vacuum filtration or in a batch centrifuge as in certain cases filtration of very fine solids from the liquor was not possible. On the other hand, the precipitated product was easily separated by using vacuum filtration.

A very critical observation from the filtration operation was that it was not possible to filter solids after the leaching of dewatered sludge as the solids are very fine and use of filter below 30 µm would result in rapid blocking of the filter. If filters above 50 µm were used, this resulted in little or no filtration at all. On the other hand, for dried and crushed sludge with particle size <5mm more than 80 % solids could be removed by filtration at 50 µm. It was also possible to filter the liquor at 25 µm with some difficulty, depending on the fraction of the very fine solids. As centrifugation of the acidic leach liquor would not be feasible, filtration was the best option for the separation of solids.

Therefore, use of dried and crushed sludge in the PULSE process enables the filtration of the solids from the leach liquor.

The dried solids after leaching and filtration, contained on average about 50% dry matter. In order to recover a part of the P and acid from the wet sludge after filtration, a washing step is implemented in the demonstrator.

In case of precipitation of product at lab scale, the product could be easily filtered by vacuum filtration with a filter of 11µm pore size.

3.4.1.4 *I3 demonstrator construction*

The construction of most of the modules of the I3 PULSE demonstrator was carried out at ULiège except for the sludge drier unit and the reactive-extraction unit, which were purchased as ready-to-use units. The modules for the other unit operations were constructed at ULiège with the help of the in-house technicians by putting together individual equipment and parts that was purchased such as tanks, filters, pumps, hoses, etc.

The I3 demonstrator was designed and built as a mobile pilot plant so that it could be transported in containers and tested at different locations within the Phos4You project The PULSE demonstrator consists of two containers which can be placed parallel and opened on the long side as well as the short side. A tent can be installed between the two containers as shown in Figure 3.4.20 in order to create an enclosed space where the mixer settlers (MS) for solvent extraction can be assembled as all the sites where the demonstrator is operated do not have an enclosed space. The other equipment modules such as drying, crushing, leaching, precipitation, and filtration are set up inside the containers as shown in Figure 3.4.21. The other container will be used for storage and transport of the MS and other utility equipment when the demonstrator has to be moved from one site to another. When the MS has been removed and installed at the site, this second container is used as a temporary office and for storage of chemical stock.

Figure 3.4.20: PULSE demonstrator construction at ULiège (Picture: ULiège/Z. Shariff).

Figure 3.4.21: PULSE demonstrator: drying, crushing, leaching, precipitation, and filtration modules installed inside container (Picture: ULiège/ Z. Shariff).

For the tests at ULiège, as sufficient indoor space was available at the Hall of Chemical Engineering at ULiège, it was decided to assemble the MS inside the Hall as shown in Figure 3.4.22 and Figure 3.4.23.

Figure 3.4.22: Mixer-settler equipment for solvent extraction. Installed inside the Chemical Engineering Hall of ULiège (Picture: ULiège/Z. Shariff)

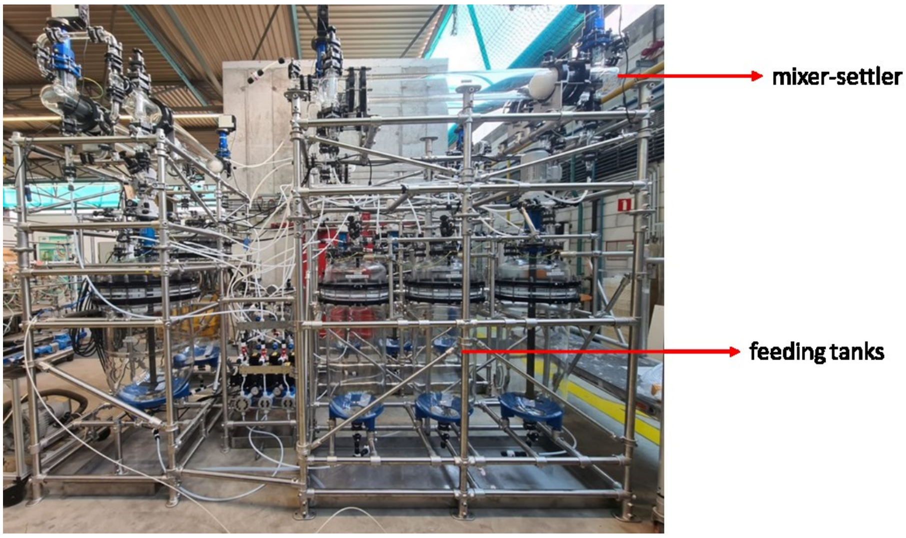


Figure 3.4.23: 5 stage mixer-settler equipment for solvent extraction tests in PULSE demonstrator (Picture: ULiège/Z. Shariff)

In a first step, the individual modules were validated and performance optimised. With the drier, more than 250 kg of dewatered sludge were dried. The drier is able to accommodate about 80 kg of sludge in a single batch and takes approximately 24 to 30 h until the sludge is completely dry.

Various configurations of leaching and filtration modules and different crushing sizes of the sludge were tested. It was found that the crushing of sludge and the fraction of fine solids had a significant impact on the filtration efficiency. The mixing of the sludge during leaching with the help of a stirrer results in attrition of solids, increasing the fraction of very fine particles. This leads to significant problems, if a good filtration is desired. From preliminary tests, it was found that after a coarse filtration using an 800 µm filter and a settling time of about 15 to 20 min, it was possible remove more than 95 % of the solids, however, further purification was difficult with a conventional filtration system due to rapid blocking of the filter by the fine particles.

With the valuable input from the experienced technical staff at ULiège, an innovative method to carry out the leaching and filtration operation in a single step was implemented in PULSE process which was validated subsequently. Three parallel leaching tanks are used in the PUSLE demonstrator as shown in Figure 3.4.24.The leaching process is repeated until a predefined S/L ratio for the leaching operation has been reached. If required, the acid solution after leaching is subjected to pressurized filtration step in order to remove any fine solids that may have escaped the filter bag during leaching.

Figure 3.4.24 Tanks used for leaching and precipitation in I3 demonstrator (Picture: ULiège/Z. Shariff)

Preliminary tests for reactive extraction were carried out in 4-stage horizontal mixer-settler unit. The start-up and the feeding of the different phases to the mixing zone of the mixer-settlers was optimised as it determines the direction of dispersion of the phases which is very critical for phase separation and to prevent crud formation. During regeneration, when the solvent loaded with metals comes in contact with the alkaline solution, a large part of the metals precipitate. The precipitated metals collect at the bottom of the settler which then causes problems with the flow and the phase separation. Therefore, some improvements were made to prevent the solid from accumulation in the settler. Further, batch-wise regeneration in tanks was also tested as a semi-continuous alternative option to continuous regeneration of the solvent in mixer-settler.

The same tanks that are used for leaching are also used to carry out precipitation. Preliminary tests were carried out for filtration of the precipitated solids using pressurized filters units which can be fitted with filter bags of different pore sizes as shown in Figure 3.4.25. Filter bags of 10 and 25 µm were used for the tests. The 10 µm filter bags were clogged very quickly and had to be emptied after filtering a small volume of mixture. The 25 µm filter bags were able to filter a volume of about 7 to 10 l before they had to be emptied. Two parallel pressurized filtration units are used in the PULSE process demonstrator.

Figure 3.4.25: Pressurized bag filtration module and filter bag of 25 µm (Picture: ULiège/Z. Shariff)

3.4.2 Execution of I3

I3 was originally intended to be tested in Belgium, Germany, Scotland and Ireland with support from the Phos4You project partners. For each location, the demonstrator was planned to be operated for about 4 weeks. But due to the delays caused by COVID 19 pandemic and administrative constraints and challenges, the operation of the demonstrator in Ireland had to be abandoned. Further due the same reasons, instead of moving the demonstrator to Germany, sludge from Germany was shipped to Belgium and the demonstrator was operated with German sludge at the Chemical Engineering Hall of ULiège.

3.4.2.1 *I3 operation with German sludge*

Sludge from Dortmund-Deusen WWTP (700,000 PE capacity) was used for demonstrator tests. Approximately 340 kg of anaerobically stabilized and dewatered sludge was received from the German partners in 2 batches in December 2020 and in January 2021.

Before the demonstrator operation, laboratory experiments were conducted and simulations with the SLLE tool were performed in order to find optimal operating parameters for the operation of the demonstrator. The dewatered German sludge had DM content of 23 % (±0.2 %) and total P content of 3.47 %. The sludge was dried to obtain 78.2 kg of dry solids with a DM content of 98.32 % and crushed to a 2 mm particle size.

The dried and crushed sludge was leached using 2 mol/L hydrochloric acid and S/L ratio of 0.25. For operation, the filter cartridge was filled with 3.3 kg of dry sludge and immersed in tank containing 40 l of HCl solution. After the desired leaching time, the used sludge was replaced with new batch of sludge until the S/L corresponded to 0.25 or 10 kg of sludge for 40 l of acid solution. Each cartridge of used sludge is subjected to washing with tap water and about 20 l of water is used to wash the 10 kg of solids. From 312 l of HCl solution about 264 l of pregnant liquor which includes the washing water was produced. The leached and washed solids have a DM matter content of about 50 %. Figure 3.4.26 shows the comparison of P leaching efficiency between the SLLE tool, lab experiments and the demonstrator test. With the demonstrator, a maximum P leaching efficiency of about 75 % was achieved. During the leaching operation it was noticed that the wetting of the sludge inside the cartridge by the acid was not uniform, which resulted in lower leaching efficiencies initially. Therefore, modifications were made to improve the wetting of the sludge and the leaching efficiency.

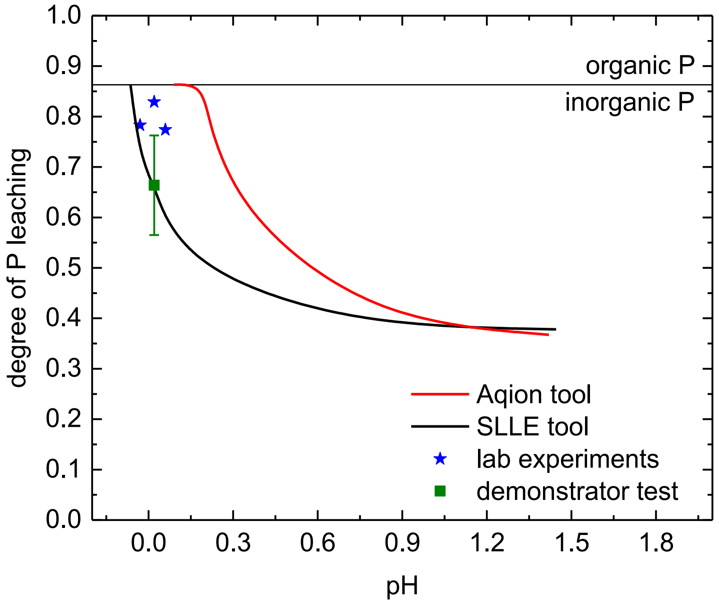


Figure 3.4.26: Comparison of P leaching efficiencies between SLLE tool, lab experiments and demonstrator tests using HCl acid

As a fraction of the leach liquor and hence the P remains in the solids after filtration, the effective recovery percentage of P from leaching and filtration operation is lower than the leaching efficiency. Without a washing step, the P recovery from leaching and filtration operation was about 53% and with the implementation of a washing step the overall recovery could be increased by about 15 % to give a maximum overall P recovery rate of 68 % from the leaching and filtration operation.

For extraction of metals, 150L of organic solvent containing 10 % Alamine 336, 10 % TBP, 3 % Exxal and 77 % Ketrul was used. The extraction of metals from the leach liquor was performed in a 2-stage counter-current operation at O/A phase ratios of 1.4, 2 and 2.8. The solvent was recycled within the system after regeneration. A protonation step is required for the Alamine 336 which is achieved by contacting the solvent with an acid solution prior to the extraction step. Therefore, 35 l of 2 mol/L HCl solution was prepared and used for protonation and the O/A phase ratio was fixed to 4. The acid solution was also recycled in the system and the pH of this solution was checked regularly. When the pH of the solution increased above 0.5, conc. HCl was added to make-up for the consumed acid.

The solvent was regenerated using an alkaline solution containing 1.5 mol/L of ammonium bicarbonate (NH_4HCO_3) and 3.5 mol/L of ammonia (NH_4OH). The O/A ratio for regeneration of solvent was fixed to 4. The regeneration of solvent was tested both continuously in the mixer-settler and also as a semi-continuous operation in a 100l glass tank.

The overall degree of metals extracted from the leach liquor is shown in Figure 3.4.27. The degree of extraction is well predicted with the SLLE tool. The change in concentration of P in the leach liquor before and after extraction was about 5% only.

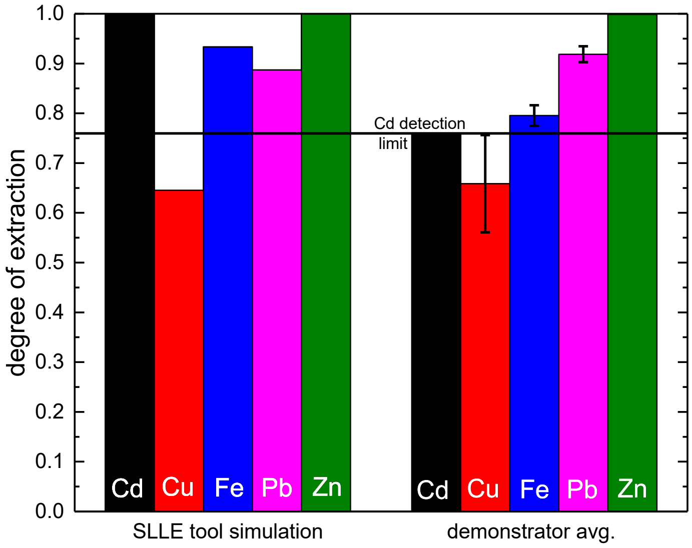


Figure 3.4.27: SLLE tool v/s demonstrator average degree of extraction of metals from German sludge liquor from a 2-stage counter-current operation at different O/A phase ratios

Finally, for the product precipitation, it was estimated that all the P is precipitated from the leach liquor at pH between 5 and 6 using the SLLE tool. Therefore after metal extraction, the pH of leach liquor was adjusted from 0.19 to between 5 and 6 by adding 25% $Ca(OH)_2$ slurry. About 0.15 l to 0.18 l of 25% $Ca(OH)_2$ slurry per litre of leach liquor was required to increase the pH to about 5.5. After pH adjustment, the mixture was stirred for about 30 minutes and then passed through a 25 µm pressurized filtration unit. The overall efficiency of the precipitation and filtration step was ≤ 90%.

3.4.2.2 *I3 operation with Belgian sludge*

After the tests with German sludge, the I3 PULSE demonstrator was transported and assembled as shown in Figure 3.4.28 in Oupeye WWTP (438,000 PE capacity) near Liège. The demonstrator was operated at this site for a month (April -May 2021) and about 280 kg of dewatered sludge was treated. Before the demonstrator operation, laboratory experiments and simulations with the SLLE tool were performed in order to optimise operating parameters for the demonstrator for the specific properties of the sludge. The Oupeye sludge was undigested and had a DM content of 21 % (±0.5 %) and total P content of ~1.72 %. The sludge was dried to obtain about 60 kg of dried sludge with a DM content of ≤95 %.

Figure 3.4.28: I3 PULSE demonstrator at Oupeye WWTP (Picture: ©ULiège-Michel Houet)

SLLE tool simulations estimated that pH lower than 0.2 was sufficient to dissolve the inorganic P or acid soluble fraction of P from the dried sludge. Therefore, dried sludge was leached using 1.5 mol/L hydrochloric acid and S/L ratio of 0.25. About 240 l of HCl solution was used and about 220 l of pregnant leaching liquor was produced. For operation, the filter cartridge was filled with 2.5 kg of dry sludge. Figure 3.4.29 shows the comparison of P leaching efficiency between the SLLE tool, lab experiments and the demonstrator test.

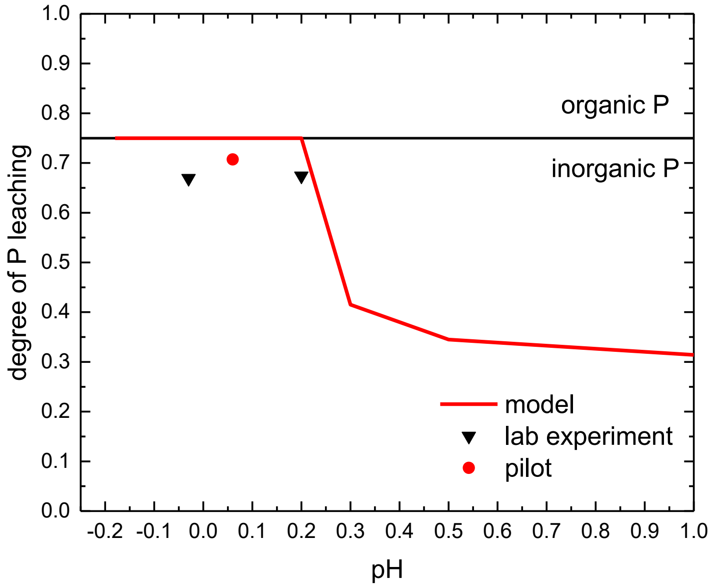


Figure 3.4.29: Comparison of P leaching efficiencies between SLLE tool, lab experiments and demonstrator tests using HCl acid

After leaching, the extraction of metals was carried out for two different O/A phase ratios i.e. 1.1 and 1.5. The solvent used for the extraction was the regenerated solvent from the tests with German sludge. The extraction efficiency of metals from the pilot tests and the SLLE tool is shown in Figure 3.4.30.

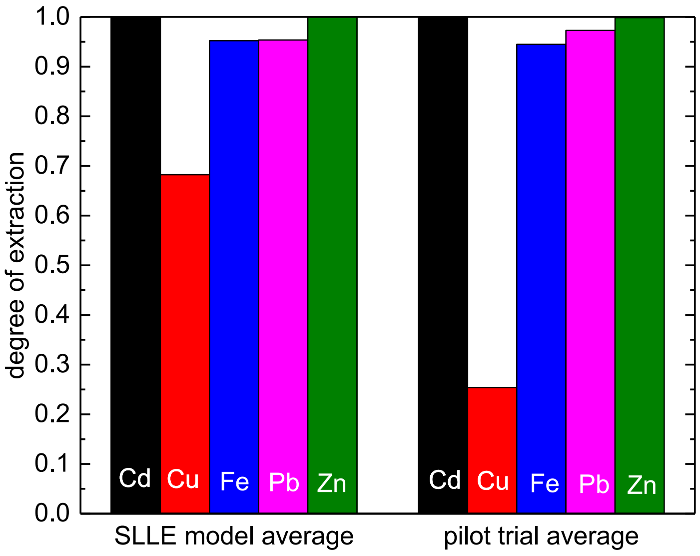


Figure 3.4.30: SLLE tool v/s pilot trial average degree of extraction of metals from Oupeye sludge liquor from a 2-stage counter-current operation

The precipitation of P from the extracted leach liquor was carried out at a pH between 5 and 6. Different combinations of 5 mol/L NaOH and 25% slurry of $Ca(OH)_2$ were used to raise the pH of the leach liquor to the desired value to see its effect on the P fraction in the final product. The precipitated solids were filtered in a pressurized bag filtration unit with a pore size of 25µ as shown in Figure 3.4.31. The overall efficiency of the precipitation and filtration step was ≤ 90%.

Figure 3.4.31: Filter bag containing the filter cake (Picture: ULiege/Z.Shariff)

3.4.2.3 *I3 operation with Scottish sludge*

The PULSE mobile demonstrator was transported and assembled at the Waste-Water development center facility of Scottish Water in Bo'ness (Scotland) to carry out trials with Scottish sludge as shown in Figure 3.4.32. The sludge was sourced from the Sterling waste-water treatment plant managed by Scottish Water.

Figure 3.4.32: PULSE demonstrator trial at waste-water Development Centre of Scottish Water in Bo'ness (Picture: ULiège/Z. Shariff)

The trials were carried during June – July 2021 for about 4 weeks which included the assembly and the disassembly of the demonstrator. About 290 kg of dewatered sludge was dried for the trial. For the trial, 70 kg of dried sludge with a dry matter content of ≤ 95 % was leached using hydrochloric acid and about 210 l of pregnant leaching liquor was produced. Figure 3.4.33 shows the comparison of P leaching efficiency between the SLLE tool, lab experiments and the demonstrator test.

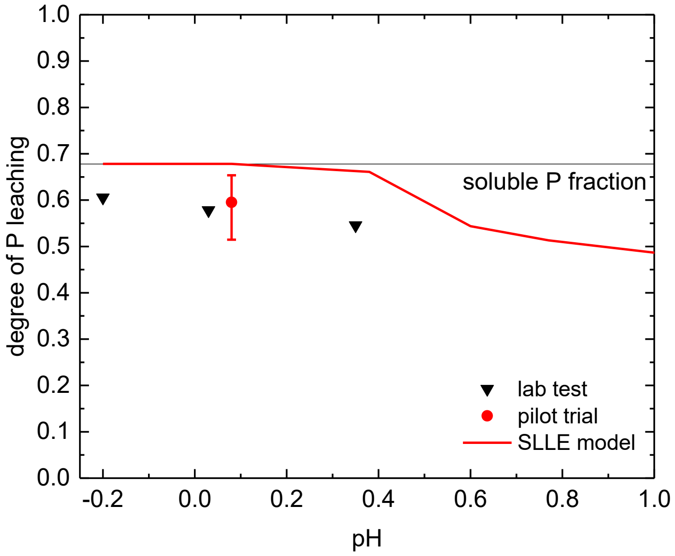


Figure 3.4.33: Comparison of P leaching efficiencies between SLLE tool, lab experiments and demonstrator tests using HCl acid

After leaching, the extraction of metals by the organic solvent was carried out in two counter-current stages. Organic solvent of a different composition compared to that used in the German and Belgian sludge trials was used. The solvent was composed of 8 % Alamine 336, 10 % TBP, 3 % Exxal and 79 % Ketrul. The O/A phase ratios of 1.25 and 1.5 were tested during extraction. The solvent stripping and protonation were carried in the same manner as described in the German sludge trials. The extraction efficiency of metals from the pilot tests and that computed with SLLE tool is shown in Figure 3.4.34. There was no change in concentration of P in leach liquor before and after solvent extraction meaning the P was not extracted.

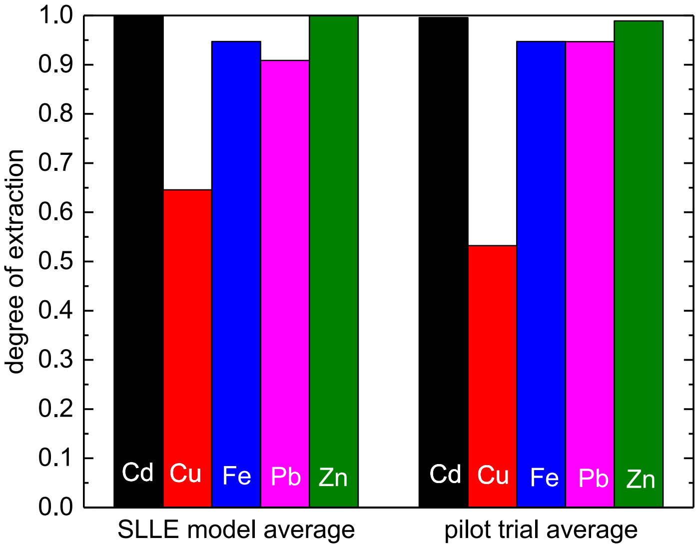


Figure 3.4.34: SLLE tool v/s pilot trial avg. degree of extraction of metals from Scottish sludge liquor from a 2-stage counter-current operation

The precipitation of P from the extracted leach liquor was carried out by adjusting the pH using combination of NaOH and $Ca(OH)_2$. Two trials were conducted where different fractions of $Ca(OH)_2$ and NaOH were used to increase the pH of the leach liquor from about 0.2 to 5.5.The precipitated solids were filtered in a pressurized bag filtration unit. The overall efficiency of the precipitation and filtration step was ≤ 85%.

3.4.3 Analyses of results of I3 operation

3.4.3.1 *Results of I3 operation with German sludge*

From the 78.2 kg of dried sludge that was treated in the PULSE demonstrator about 14 kg of product was obtained. The product obtained before and after drying is shown in Figure 3.4.35

Figure 3.4.35: PULSE product during demonstrator trial with German sludge

The overall P recovery in the demonstrator test was about 60 to 65 %. The concentrations of the various components in the intermediate stages of the PULSE process and the product obtained are listed in Table 3.4.2.

Table 3.4.2: Composition of different intermediate streams of the I3 demonstrator during operation with German sludge

		dry sludge	leach liquor before extraction	leach liquor after extraction	leach liquor after precip. at pH 5.8	PULSE product
Al	ppm	14,400	1,190	1,220	1.76	24,767
As	ppm	8.99	0.798	0.7735	0.5	9.43
Ca	ppm	26,200	5,820	5,660	18,500	19,6428
Cd	ppm	1	0.208	0.05	0.5	0.14
Cl	ppm	n/a	n/a	n/a	n/a	93,300
Co	ppm	9.44	0.953	0.9355	0.377	n/a
Cr	ppm	49.7	3.42	3.345	0.5	49.7
carbon total	ppm	n/a	n/a	n/a	n/a	31,100
Cu	ppm	515	82.9	28.3	3.83	244
Fe	ppm	56,500	9,200	1,850	18	36,000
Hg	ppm	0.529	< 0.02	<0.02	<0.02	n/a
K	ppm	4,220	379	359	278	1,910
Mg	ppm	6,820	1,100	1,045	989	3,514
Mn	ppm	718	176	170	27.8	n/a
Na	ppm	632	132	138.5	152	513
Ni	ppm	34.9	3.9	3.58	2.24	n/a
P	ppm	34,700	6,450	6,110	44.1	11,9650
P_2O_5 T	%	n/a	n/a	n/a	n/a	27.4
Pb	ppm	51	11.2	0.9115	0.15	14.1
Zn	ppm	1,100	231	0.3	0.15	12.5

3.4.3.2 *Results of I3 operation with Belgian sludge*

From the 60 kg of dried sludge that was treated in the PULSE demonstrator about 6.8 kg of product was obtained. The concentrations of the various components in the intermediate stages of the PULSE process are listed in Table 3.4.3. The overall P recovery in the demonstrator test was between 60 to 65 %. The detailed analysis of the product and the different inorganic components was not yet available at the time of preparation of this report.

Table 3.4.3: Composition of different intermediate streams of the I3 demonstrator during operation with Scottish sludge

		dry sludge	leach liquor before extraction	leach liquor after extraction	leach liquor after precip. at pH 5.6	PULSE product
Al	ppm	14600.0	458.0	471.0	< 20	
As	ppm	10.5	0.7	0.7	0.5	
Ca	ppm	23200.0	5130.0	5300.0	13000.0	
Cd	ppm	3.3	0.5	< 0.0005	< 0.0005	
Cl	ppm	n/a	n/a	n/a	n/a	
Co	ppm	5.3	0.4	0.5	< 1	
Cr	ppm	106.0	13.3	13.6	0.3	
carbon total	ppm	n/a	n/a	n/a	n/a	
Cu	ppm	266.0	30.0	22.2	7.2	
Fe	ppm	26120.0	3120.0	551.0	< 3	
Hg	ppm	0.9	0.0014	0.0002	< 0.0002	
K	ppm	7830.0	1120.0	1140.0	980.0	
Mg	ppm	5650.0	811.0	837.0	864.0	
Mn	ppm	437.0	99.4	112.0	19.4	
Na	ppm	990.0	346.0	359.0	7490.0	
Ni	ppm	31.4	3.8	3.9	2.7	
P	ppm	17600.0	3190.0	3250.0	217.0	
P_2O_5 T	%	n/a	n/a	n/a	n/a	
Pb	ppm	141.0	25.3	1.2	< 3	
Zn	ppm	1260.0	195.0	0.6	< 3	

3.4.3.3 *Results of I3 operation with Scottish sludge*

From the 70 kg of dried sludge that was treated in the PULSE demonstrator about 3.3 kg of product was obtained. The overall P recovery in the demonstrator test was between 48 to 52 %. The concentrations of the various components in the intermediate stages of the PULSE process and the product obtained are shown in Table 3.4.4.

Table 3.4.4: Composition of different intermediate streams of the I3 demonstrator during operation with Scottish sludge

		dry sludge	leach liquor before extraction	leach liquor after extraction	leach liquor after precip. at pH 5.8	PULSE product
Al	ppm	n/a	898.0	880.0	< 5	n/a
As	ppm	4.4	0.428	0.8	0.3	5.6
Ca	ppm	15459	3586.3	3522.096	8510.0	140103.0
Cd	ppm	0.8	0.133	< 0.0005	< 0.0005	< 0.1
Cl	ppm	n/a	n/a	n/a	n/a	n/a
Co	ppm	n/a	0.2	0.2	< 0.25	n/a
Cr	ppm	45.2	2.5	2.5	< 0.25	76.7
carbon total	ppm	n/a	n/a	n/a	n/a	n/a
Cu	ppm	130.8	16.9	7.89	4.6	148.0
Fe	ppm	n/a	1660.0	88.0	< 0.75	n/a
Hg	ppm	0.73	0.001	< 0.0002	< 0.0002	<0.5
K	ppm	2761	196	197	230.0	1690.0
Mg	ppm	6332	494.74	495.88	466.0	3476.0
Mn	ppm	282.8	47.9	47.634	466.0	909.0
Na	ppm	n/a	155.0	218.819	13300.0	75005.0
Ni	ppm	21.4	1.5	1.5	1.2	7.7
P	ppm	12831.0	1868.0	1826.237	256.0	108713
P_2O_5 T	%	n/a	n/a	n/a	n/a	24.8
Pb	ppm	121.5	18.9	1.007	< 0.75	55.3
Zn	ppm	613.7	92.276	<0.3	< 0.75	<15

3.4.3.4 *LCA for I3*

The PULSE process has been included in the LCA-LCC works done within Phos4You. See chapter 5.

3.4.4 Discussion of results for I3 operation

The I3 PULSE demonstrator was first operated with the German sludge. An overall P-recovery efficiency between 60 to 65 % was obtained for this trial. The P-recovery efficiency in the PULSE process is largely dependent on the leaching operation. It was observed that during the leaching, the wetting of the dried sludge was not optimum and hence the dissolution of P also. After making some modifications to the leaching module, the P dissolution was found to increase. Therefore, in principle it is possible to further improve the overall P-recovery of the PULSE process. The extraction of metals in the solvent extraction step was carried out as expected based on the lab trials. During the regeneration of the solvent, the metals that are stripped from the organic phase precipitate in the aqueous phase which leads to a small amount of solvent being trapped in the precipitate. As a result, phase separation in the continuous horizontal mixer was not optimum. Alternatively, the regeneration of the solvent was also carried out semi continuously in a tank. In a large-scale operation, a vertical settler may be used to sperate the organic phase and the mixture of metal precipitate and the basic aqueous solution. The metal precipitate contains about 50 % Fe by mass which can be further separated from the stripping phase by filtration or settling and the stripping solution can be reused. After precipitation, the final product from the German sludge trials was supplied to Prayon S.A. to perform analysis and granulation tests. The composition of the final product is listed in Table 3.4.2. Based on the feedback of Prayon S.A., the P_2O_5 content of 27% in the PULSE product obtained from German sludge corresponded to the P_2O_5 content of their own fertiliser product. Granulation tests were performed in order to check if the PULSE product could be directly blended with the commercial fertiliser as shown in Figure 3.4.36.

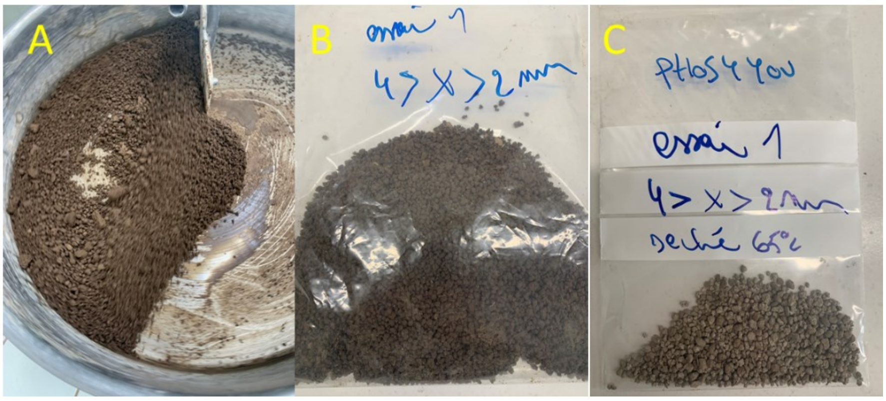


Figure 3.4.36: Granulation tests by Prayon S.A. on the PULSE product obtained from German sludge. A - during granulation; B - granulated product wet; C- granulated product dry (Picture: Prayon S.A.)

The granulation tests for PULSE product were satisfactory meaning the dried PULSE product can be milled, blended with the commercial fertiliser, and then granulated. The total carbon content of the product is only harmful in case of traces of organic solvents or toxic organic compounds. An organic analysis carried out by the quality assessment team of the Phos4You project on a previously produced PULSE product sample at semi-pilot scale from Oupeye sludge did not detect any harmful organic compounds (Bogdan et al. 2021).

The total P concentration of sludge from Oupeye wwtp in Belgium and Sterling wwtp in Scotland were much lower compared to that of the German sludge. The acid-soluble P fraction of the two sludges was also lower and therefore correspondingly lesser amounts of product was produced during the trials.

3.4.5 Conclusion for I3

Based on the results of leaching wet and dried sludge, it can be concluded that there was no significant difference in the leaching efficiency of P. In principal, acidic leaching dissolves mostly the inorganic fraction of P from the sludge and this dissolution is dependent on the pH. Dried sludge is easier to handle and also the solids liquid separation after leaching is more efficient compared to wet sludge. Drying the sludge, also reduces the consumption of acid and the volumes that must be treated in the later steps.

It was observed that the inorganic or acid-soluble fraction of P was higher in the German sludge which was anaerobically stabilized sludge and therefore the leaching efficiency is also higher.

During solvent extraction, the metals Fe, Cd, Hg, Pb and Zn were very well extracted and Cu was extracted moderately while the change in P concentration of the leach liquor is negligible. The solvent regeneration was very efficient, except for the issue of phase separation when the metals precipitate during regeneration with basic solution which can be optimised by quasi-continuous operation in tanks or use of vertical settlers.

The final product of the PULSE process containing calcium phosphate salts has very low concentrations of Fe, Cd, Cu, Hg, Pb and Zn. The P_2O_5 concentration of the final product depends on the base used i.e. NaOH or $Ca(OH)_2$ and also on the other precipitable components in the liquor. The overall efficiency of the P recovery from sludge in the PULSE process is between 60 to 70 %.

The P_2O_5 content of the product obtained by PULSE process is high, so that the PULSE product can be used directly as a fertiliser after milling and granulation.

After the completion of the demonstrator trials in Scotland within the Phos4You project, the demonstrator will be located at the ULiège-Sart-Tilman campus. The equipment of the demonstrator will be used to carry out scale-up studies for some of the unit operations. The ULiège team will actively explore opportunities and co-operations in order to further carry out demonstrations of the PULSE process.

Acknowledgements

We are thankful to BTC Europe GmbH for samples of Alamine336, TOTAL Belgium for samples of Ketrul D80, and Exxon Mobil for samples of Exxal 10.

We are thankful to Emschergenossenschaft / Lippeverband and Scottish Water for supplying the sludge and for supporting the PULSE demonstrator trials.

We are thankful to Faculty of Bioscience Engineering – UGhent for ICP analysis of samples and Prayon S.A. for analysis and granulation tests of the PULSE product.

4 Demonstration of solutions combining phosphorus removal and recovery

Three solutions to remove phosphorus from small-scale wastewater treatment plants, combined with the production of a recyclable material, are presented in this part.

4.1 Demonstrator I4: Microalgae to recover P from small-scale WWTPs

---

Authors: Ania Escudero, Lena-Dorothea Reichelt, Ole Pahl (GCU)

Phosphorus (P) ends up in the water through different processes. One major input is agriculture. The overuse of phosphate fertilisers leads to accumulation of nutrients in the soil which can be carried out into rivers and groundwater flowing into lakes or sea. The second big source of P is wastewater treatment plants (Figure 4.1.1). The discharge of untreated water leads to high loads of nutrients in water bodies (Lemley and Adams 2019; Palazzo 2010)

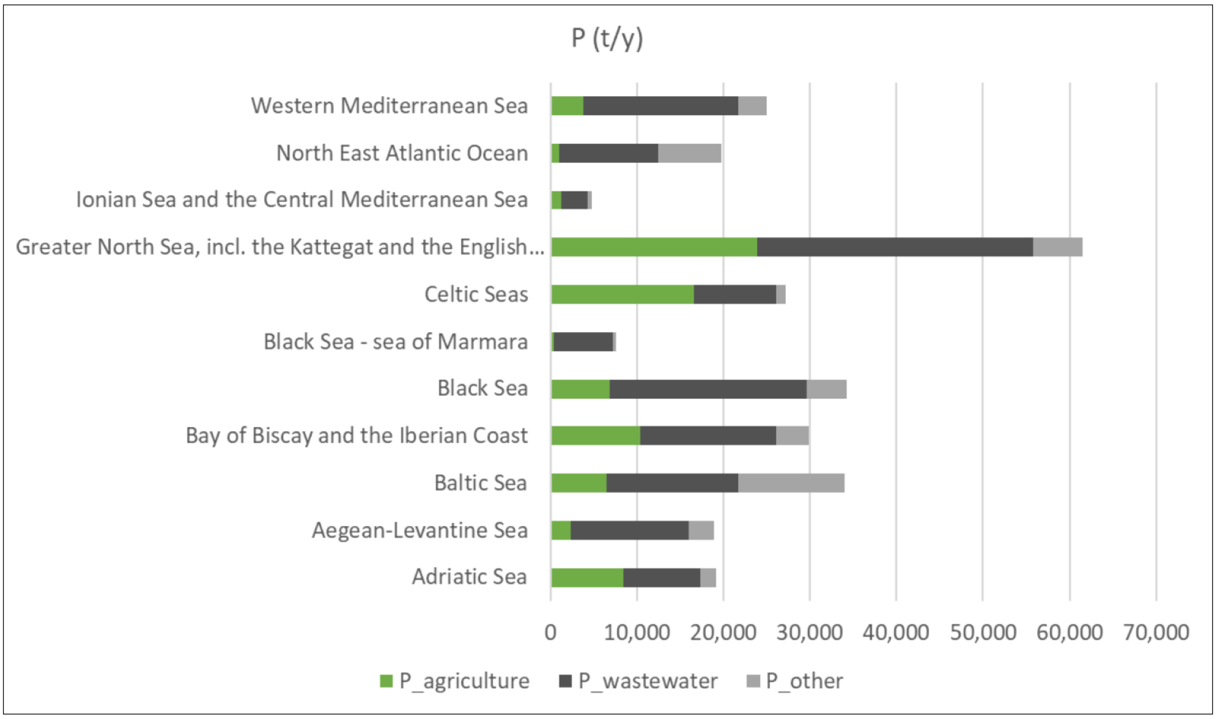


Figure 4.1.1: Loads of P to EU regional seas, by source (tonnes/year in 2014)(Pistocchi et al. 2019)

Scotland is considered as 97 % rural with around 1600 WWTP of a capacity lower than 500PE, most of them concentrated in the northern part of the country. A large part of eutrophication is caused by the insufficient treatment of wastewater in septic tanks and small wastewater treatment plants (Bunce et al. 2018, pp. 1–15; Scottish Environment Protection Agency (SEPA) 2017).

There is no clear single legislation dealing with the problem of eutrophication in the UK. The European Community's urban wastewater treatment directive aims to reduce eutrophication where discharges bring in high loads of nutrients. In the UK, to 62 rivers and canals, 13 lakes and reservoirs and 5 estuaries have been identified to be eutrophic areas (European Commission 2017b).

Phosphorus removal technologies find their origin in Switzerland in the 1950ies with phosphorus precipitation to solve the widespread problem of eutrophication (Rich 2005). This simple chemical process is now widely spread around the globe as one of the most common methods to remove P from different wastewaters. However, as the urge of recovering P from wastewater instead of removing it is getting more attention due to new regulation and legislation in place, new technologies are being developed to meet the low required concentrations. Each treatment has its own advantages and disadvantages.

In Scotland, recovering P from small, and possibly remote, sites presents several challenges as suitable systems require robustness and low maintenance plus the variability of P in wastewater is often high. The extremophilic microalgae *Chlamydomonas acidophila*, which grows at a pH of 2-3, appears to have potential for P-recovery at these sites, as it is able to recover P and N in different wastewaters at a rate of around 7 mg $L^{-1}d^{-1}$ and 9 mg $L^{-1}d^{-1}$, respectively (Escudero et al. 2014). Furthermore, this species is mixotrophic so the presence of organic carbon in the effluent improves nutrient recovery efficiency.

One of the limiting factors in microalgae technology is light availability and *C. acidophila* have shown to require a very low light intensity to grow (40-113 µmol photons $m^{-2}s^{-1}$). Additionally, the presence of micropollutants such as pharmaceuticals in urban wastewater could inhibit biological treatment processes. Here *C. acidophila* is shown to be a resistant species as it is able to grow and consume nutrients in the presence of pharmaceuticals 1000 times higher concentrations than the ones reported in these effluents (Escudero et al. 2020a).

Different experiments were carried out in order to optimise the scaling-up of this process: On the one hand the microalgae process control parameters were studied to optimise the P-recovery and cell growth efficiency; on the other hand different reactor designs were studied for this specific microalgae *Chlamydomonas acidophila*.

4.1.1 Preparation of I4

Several laboratory scale growth studies were conducted to optimise the *C. acidophila* growth and nutrients consumption and therefore improve the design of the demonstration unit. Different parameters, such as light intensity, cycles and temperature, which may impact on the ability of this alga to recover P, were evaluated.

Figure 4.1.2: Set-up of the process control parameters tests (Picture: GCU)

4.1.1.1 *Influence of light intensity on nutrients recovery*

One of the limiting factors in microalgae technology is light availability, as the adsorption of light energy is the first step of the photosynthetic process and the amount of light that is absorbed determines the efficiency at which light is converted to biochemical energy. Microalgae can be grown at various light intensities (Mooij 2016).

Chlamydomonas acidophila has excellent low light and low temperature acclimation properties that support survival of these species in extreme climate (GERLOFF-ELIAS et al. 2005).

A broad range of light intensities were evaluated in order to reduce the energy supply in the reactor: 20, 30, 50, 70, 90, 100, 160 and 270 µmol photons $m^{-2}s^{-1}$.

The results obtained in the lab showed that *C. acidophila* grows successfully under a maximum photosynthetically active radiation (PAR) light of 270 µmol photons $m^{-2}s^{-1}$, coinciding with previous studies (Nishikawa and Tominaga 2001; Cuaresma et al. 2006; GERLOFF-ELIAS et al. 2005). Furthermore, *C. acidophila* showed similar growths and nutrients consumptions at intensities higher than 50 µmol photons $m^{-2}s^{-1}$ intensities.

Usually, at low light intensities, microalgae are capable of utilising light energy at a very high efficiency. At increasing light intensities, the light use efficiency drops as the photosynthetic machinery slowly becomes oversaturated, which leads to a waste of light energy. Therefore, it seems that at intensities higher than 50-70 µmol photons $m^{-2}s^{-1}$ the photosynthesis rate is saturated, and the extra light is dissipated as heat. Thus, it seems that *Chlamydomonas acidophila* consumes nutrient more effectively at low light intensities as the highest removals were achieved at 50 µmol photons m^{-2} s^{-1} while other species perform their best at higher light intensities.

At lower intensities such as 20 and 30 µmol photons $m^{-2}s^{-1}$, the microalgae grew and consumed nutrients slightly slower than at higher intensities, which means that they are able to utilise more light energy at higher efficiencies.

Based on the obtained results, it can be concluded that *C. acidophila* requires much lower light intensities to grow and consume nutrients than other microalgae used for wastewater treatment, which leads to a lower energy consumption by the demonstration unit.

4.1.1.2 *Influence of light cycles on nutrients recovery and biomass growth*

It is acknowledged that light availability is one of the greatest challenges for microalgae cultivation and a high photosynthetic efficiency is essential to decrease the costs of microalgal biomass production. Furthermore, some researchers have found that the light/dark (L/D) cycle, in which the microalgae alternated between the light and dark, can promote the microalgae growth better than continuous light (Liao et al. 2014; Deng et al. 2019). Therefore, understanding the L/D cycle characteristics has important implications for designing effective large-scale microalgae culture systems. Although many authors have studied this parameter in different microalgae, there are no reports about the effect on *C. acidophila*. The aim of this study was to evaluate the effect of different light cycles on the growth of *C. acidophila* and phosphorus recovery rates from urban wastewater under very low light intensities.

Batch laboratory scale growth studies were conducted to evaluate the effect of different L/D cycles on the nutrient removal by *C. acidophila* from urban wastewater. Five different L/D regimes were studied: 24/0, 18/6, 12/12, 6/6 and 2/2 h. Assays were carried out using effluent taken after primary sedimentation from an urban WWTP in Paisley, Scotland. The Chemical Oxygen Demand (COD), NH_4 and PO_4 concentrations in this effluent were around 100, 17 and 7 mg L^{-1} respectively. The pH was adjusted to 3 by addition of 5N H_2SO_4 and 50 mL effluent in 250 mL glass Erlenmeyer flasks were inoculated with *C. acidophila* adjusted to approximately 1.10^6cells mL^{-1}. Flasks were place in an orbital incubator shaker at 23˚C, stirred at 100 rpm and illuminated at a rate of approximately 43 µmol photons m^{-2} s^{-1} by white LED lights. All samples were incubated in triplicate. The cell numbers, ammonium and phosphate concentration were measured every 2-3 days in each sample during the incubation period of 7 days.

The change in cell concentration and P removal are shown in Figure 4.1.3 and Figure 4.1.4. Different growth rates and P removal patterns were observed in cultures under the different L/D regimes at a light intensity of 43 µmol photons m^{-2} s^{-1}. The highest cell growth and P removal was observed under a continuous illumination, where 100 % of P was removed in 5 days, eliminating about 1.5 mg PO_4 $L^{-1}d^{-1}$ and achieving a growth rate of about 0.9 d^{-1}. At this low light intensity, *C. acidophila*´s growth rate was higher than other species used for wastewater treatment (Aslan and Kapdan 2006; Franchino et al. 2013), maybe due to the presence of about 100 mg L^{-1} of COD in the wastewater and the mixotrophic nature of *C. acidophila*, which supplements its carbon/energy budget with the osmotrophic uptake of dissolved organic carbon (Tittel et al. 2005). For some algae, mixotrophic growth results in 3–10 times more biomass production relative to phototrophy (Bhatnagar et al. 2011).

The cells growth under the 18/6 cycle was slower than in continuously lit samples, achieving the exponential growth phase about 3 days later (Figure 4.1.3). Samples illuminated for half the time, regardless the length of the photoperiod (12h, 6h or 2h), achieved a proportional growth rate equivalent to the light time, producing 50 % less biomass than under continuous illumination.

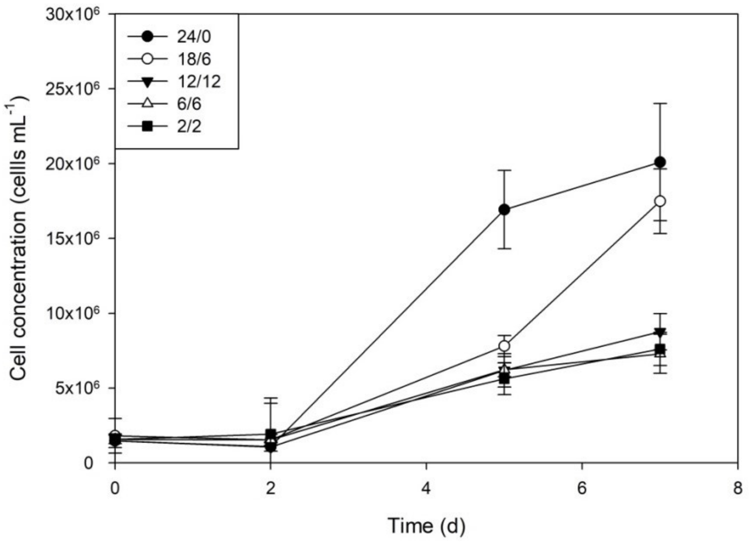


Figure 4.1.3: Changes in the cell concentration in the medium during incubation. Each point represents mean value from three replicate determinations with standard deviation

Near linear PO_4 removal was observed in all the samples except under 18/6 cycle where maximum P consumption was observed in the first 2 days of incubation (Figure 4.1.4). The P removal after 5 days of incubation was 100, 91, 75, 51 and 50 % for the cycles 24/0, 18/6, 12/12, 6/6 and 2/2 respectively. When the pH is high, orthophosphate can be easily removed from wastewater by precipitation as calcium and magnesium salts (Iasimone et al. 2018). However, in the present study, due to a low pH in the media, it can be stated that P removal was attributed to the assimilation of the microalgae. In terms of efficient utilisation of light energy, a medium photoperiod (18/6), removed 15 % more P per illumination hour than the continuous lit samples. When the light was reduced to 50 %, differences were observed with the different photoperiods. The P removal achieved with 6h and 2h photoperiods were similar to samples under continuous illumination, however, at a longer photoperiod of 12h, the light utilisation efficiency for P-recovery increased by 25 %, even though the biomass produced was lower.

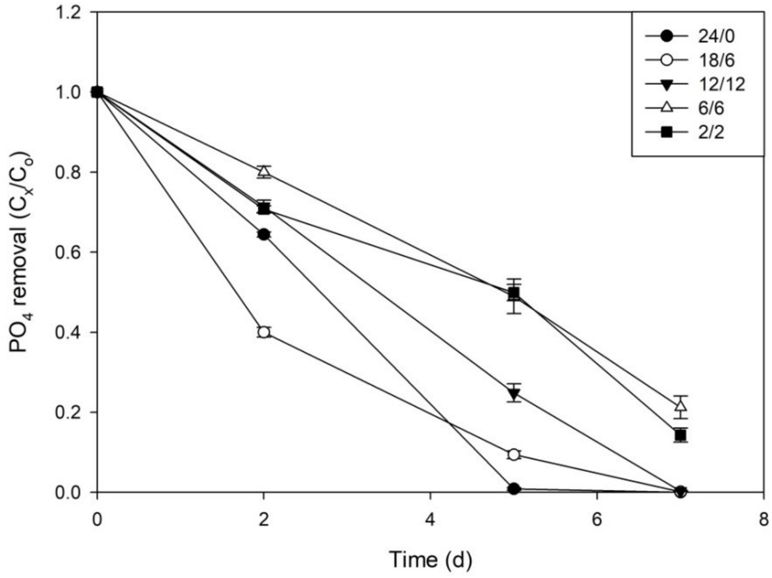


Figure 4.1.4: Removals of PO_4 in the medium during incubation, expressed as the ratio between the PO_4 concentrations in the media (C_x) and the initial PO_4 concentration (C_0). Each point represents mean value from three replicate determinations with standard deviation

Based on the results obtained in this study, it can be concluded that *C. acidophila* grows and consumes nutrients at low light intensities and that the P removal efficiency is improved using 18/6 or 12/12 L/D regimes. Further research is required to study the long-term effect of these different light frequencies and to optimise the process.

4.1.1.3 *Influence of temperature and light intensity combination on nutrients recovery and cells growth*

The growth rate of microalgae and their efficiency in wastewater remediation is highly influenced by light and temperature conditions. Light is the main energy source in photochemical reactions and temperature influences macromolecular structures, energy absorption and consumption, as well as the functioning of photosynthetic and metabolic enzymes (Ferro et al. 2018). Photo-inhibition is a function of temperature and shows a coupled response with photorespiratory carbon metabolism (Kim and Lee 2001) and therefore, the effect of the combination of different light intensities at different temperatures on the growth and nutrient consumption by *Chlamydomonas acidophila* in urban wastewater should been studied in order to evaluate the most cost effective and efficient values of these two parameters in combination.

Four batch experiments were carried out at different temperatures (16, 20, 25 and 30 °C) and light intensities (15, 40 and 172 µmol photons $m^{-2}s^{-1}$) and the results are shown in Figure 4.1.5 and Figure 4.1.6.

Chlamydomonas acidophila is an extremophilic species known for requiring low light intensities to grow and consume nutrients. Based on the results obtained in these experiments, it seems that the microalgae recover more PO_4 under a lower light intensity of 40 µmol photons $m^{-2}s^{-1}$ than 172 µmol photons $m^{-2}s^{-1}$ irrespective of the incubation temperature. Usually, at low light intensities, microalgae are capable of utilising light energy at a very high efficiency. At increasing light intensities, the light use efficiency drops as the photosynthetic machinery slowly becomes oversaturated, which leads to a waste of light energy. Therefore, the microalgae grew and consumed nutrients slightly slower than at higher intensities, which means that they are able to utilise more light energy at higher efficiencies.

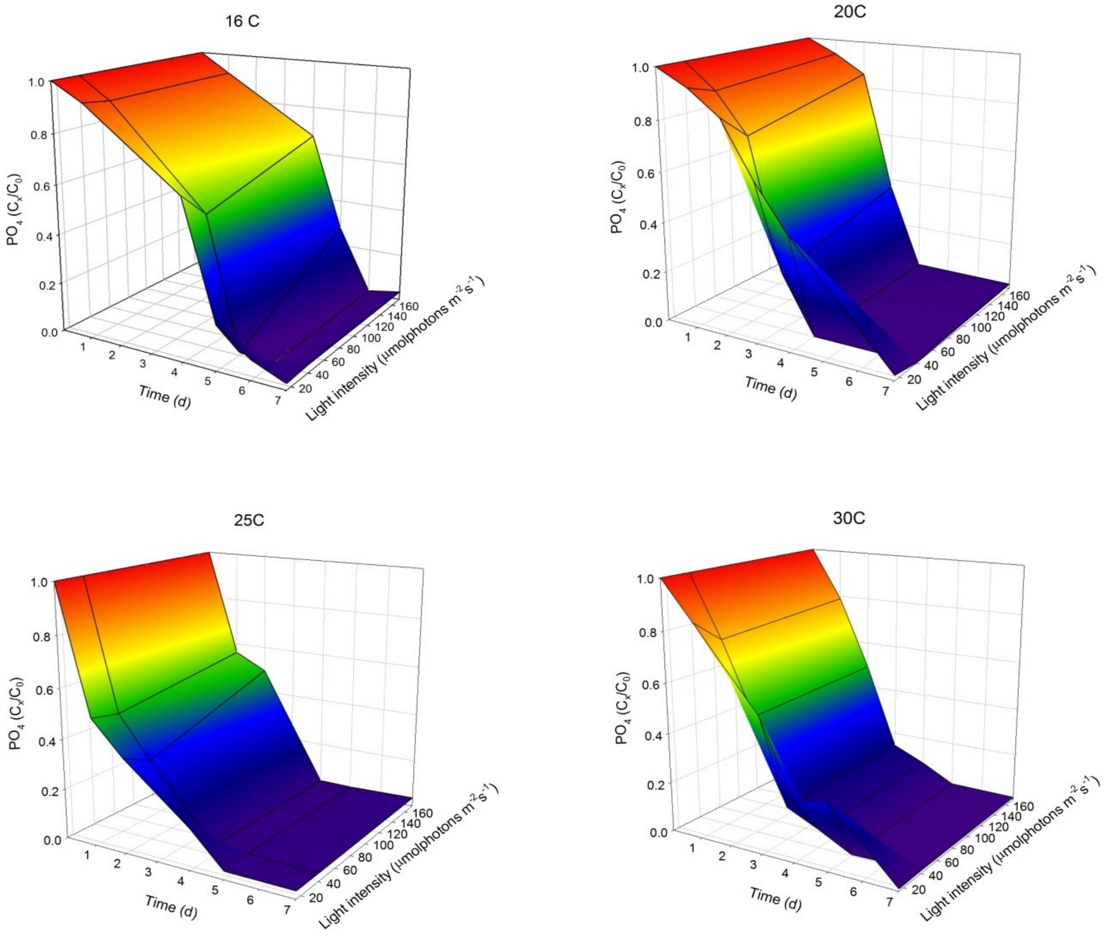


Figure 4.1.5: Removals of PO_4 in the medium during incubation at different light intensities and different temperatures, expressed as the ratio between the PO_4 concentrations in the media (C_x) and the initial PO_4 concentration (C_0)

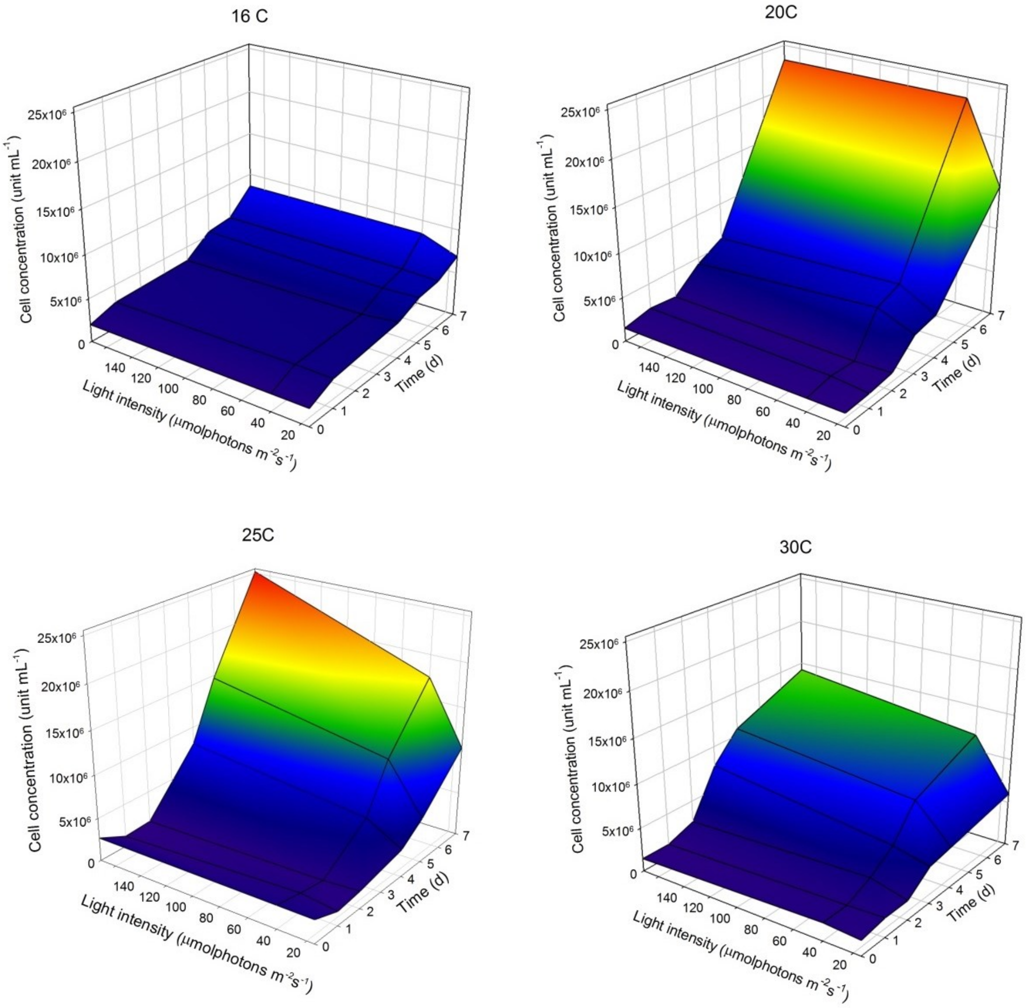


Figure 4.1.6: Changes in the cell concentration in the medium during incubation at different light intensities and different temperatures

Temperature may play a key role in photo-inhibition, which is known to impact algal growth rate as temperature stress leads to changes in cytoplasmic viscosity and is responsible for less efficient carbon and nitrogen utilisation (Venkata Subhash et al. 2014). This stress can be observed both at low and high temperatures (16 and 30 °C) where the cell growths were low regardless the light intensity applied. Under stress, the cell division is one of the processes that microalgae suppress in order to survive and that is the reason why the cells consumed P even though the cells number did not increase in the media. These results coincide with other studies where the growth rates of the microalgae increase with the increase in temperature up to its optimum and once it reaches its optimum, growth rate decreases (Venkata Subhash et al. 2014).

Differences in cell growth between applying 172 or 40 µmol photons $m^{-2}s^{-1}$ were observed at 25 °C where the growth was higher at higher light intensities. Previous studies indicated that light with low intensity could cause growth limitations and that the increase in temperature above its optimum inhibits the cells growth (Chen et al. 2016). Therefore, it seems that the combination of 2 slight stresses (a slightly higher T than optimal together with a slight low light intensity) is the reason for the cells to grow slower at under 40 than 172 µmol photons $m^{-2}s^{-1}$ at 25 °C.

The optimum cell growth and nutrient consumption was achieved at 20 °C under a light intensity of 40 µmol photons $m\text{-}^{2}s^{-1}$.

Therefore, it seems that *C. acidophila* requires much lower light intensities and temperatures to grow and consume nutrients than other microalgae used for wastewater treatment, which leads to a lower energy consumption by the demonstration unit.

4.1.1.4 *Influence of semi-continuous wastewater treatment by Chlamydomonas acidophila (10L tanks - lab experiments)*

Wastewater samples were collected from the small scale local WWTP Laighpark (Scotland) and tests were carried out to evaluate the behaviour of the microalgae in the presence of settled (effluent after the primary treatment) and final (effluent after secondary treatment) wastewater in a semi-continuous experiment. The characteristics of the effluents were the following:

Table 4.1.1: Characteristics of small scale WWTP's wastewaters used to evaluate the behaviour of the microalgae

	Settled effluent (After Primary treatment)	Final effluent (After Secondary treatment)
P-PO_4 (mg/L)	1 – 5	1 – 5
COD (mg/L)	90 – 215	25 – 35
NH_4 (mg/L)	12 – 33	1 – 5
NO_3 (mg/L)	0.3 – 1.3	10 – 40
pH	5.8 – 6.5	5.8 – 6.5

Two 10 L tanks were set-up to compare the semi-continuous addition of the two wastewaters to the microalgae species *Chlamydomonas acidophila*. One reactor was fed with settled effluent and the other one with final effluent with a hydraulic retention time (HRT) of 3 days and a flow of 139 mL h^{-1} every 120 minutes for two hours. The HRT was

decreased to 2 days after 50 days when the reactor was stable. The reactor was continuously illuminated at a rate of approximately 70 µmol photons $m^{-2}s^{-1}$ at the tanks surface. The mixing was ensured by air stones and NO_3, NH_4, PO_4 and pH were monitored on a daily basis. Sulfuric acid was added to the wastewater to adjust the pH to 3.

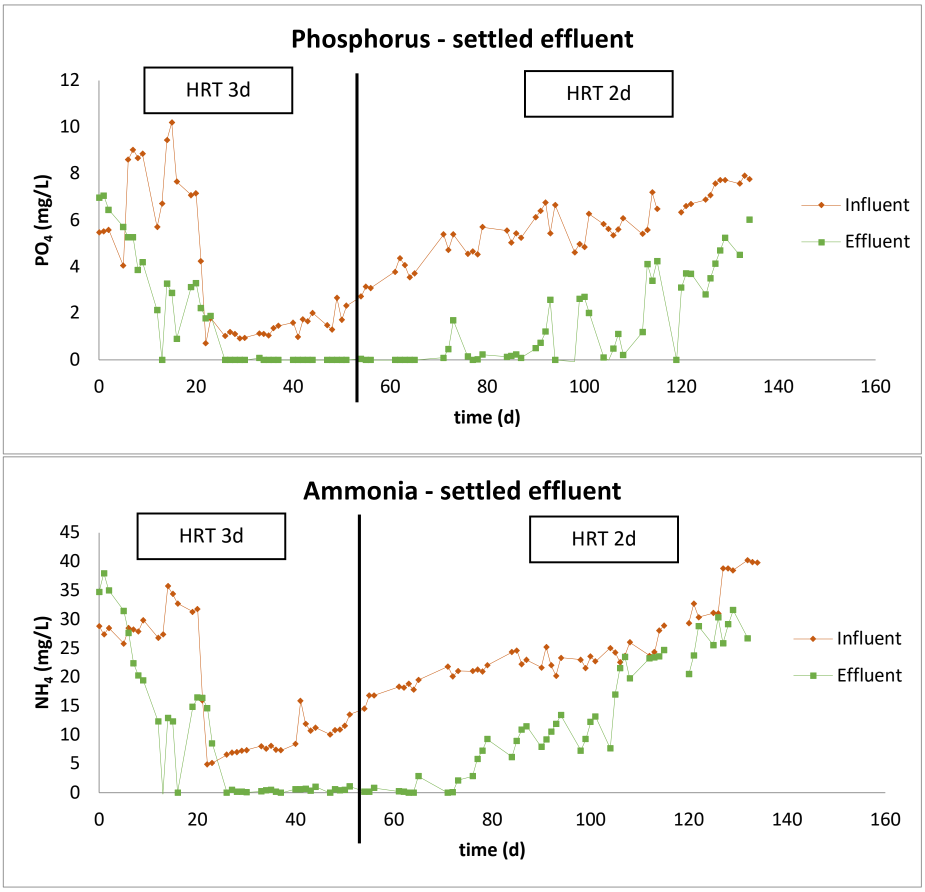


Figure 4.1.7: Changes in NH_4 and PO_4 concentrations in the influent and effluent during the experiment. Each point represents mean value from three replicate determinations with standard deviation

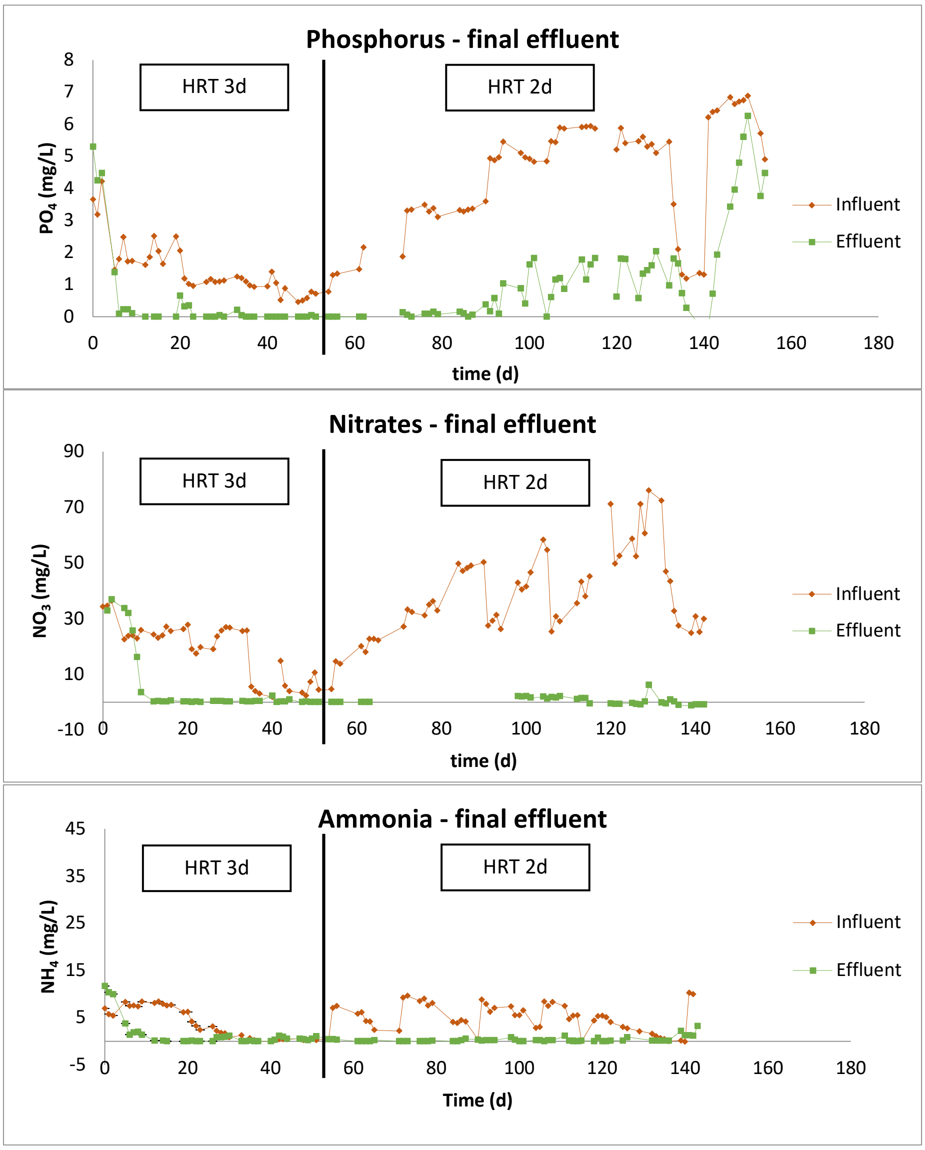


Figure 4.1.8: Changes in NO_3, NH_4 and PO_4 concentrations in the influent and effluent during the experiment. Each point represents mean value from three replicate determinations with standard deviation

A pH-dependent equilibrium exists between the soluble ammonium ion (NH_4^+) and dissolved molecular ammonia (NH_3). High pH favours ammonia volatilization by driving the equilibrium between NH_3 and NH_4^+ to molecular ammonia (Lin et al. 2009). Also, when the pH is high, phosphate can be easily removed from wastewater by precipitation as calcium and magnesium salts (Martínez 2000; Iasimone et al. 2018). In the present study, the pH remained below 3 in all samples during the incubation. Therefore, it can be assumed that any decrease in nutrients concentration in the rest of the samples was entirely attributed to their assimilation by microalgae.

Both tanks seem to recover N and P adequately, removing 100 % of these compounds during 50 days of experiment. The microalgae needed around 6 day to acclimatize and start consuming nutrients. After this start-up period, recovery values of around 10 mg NH_4 $L^{-1}d^{-1}$ and 2.5 mg PO_4 $L^{-1}d^{-1}$ and 20 mg NO_3 $L^{-1}d^{-1}$ and 1.5 mg PO_4 $L^{-1}d^{-1}$ were achieved in the tank fed with settled effluent and final effluent. The ammonium removal efficiencies using *C. acidophila* are higher than those reported in studies with other microalga and in which the pH was maintained below 7, and therefore ammonia volatization and phosphate precipitation was controlled (Aslan and Kapdan 2006; Franchino et al. 2013).

A reduction of HRT to 2d and an increase in the nutrient concentration in wastewater derived in a non-complete nutrient removal from wastewater. However, the recovery rates were higher due to a higher concentration of nutrients in influent wastewaters.

In summary, *C. acidophila* appears to be a promising agent for long-term treatment of wastewater effluents and therefore for pilot-scale trials.

4.1.2 Execution of I4

In order to test the suitability of an existing photobioreactor (PBR) to grow *Chlamydomonas acidophila* to investigate scale-up for wastewater treatment, two suspended cells reactor designs were selected to compare the performance on recovering P of the two technologies:

- 500 L self-cleaning photobioreactor which does not require aeration and incorporates a high surface area LED lighting and external heat exchanger (Designed and manufactured by Greenskill Environmental Technology Ltd.).
- 700 L air lift photobioreactor operated via a controller that allows adjusting the temperature, the pH and the light intensity (Designed and manufactured by Xanthella Ltd.).

A preliminary three-month trial was carried out, where the growth of *Chlamydomonas acidophila* in these two PBRs was tested and several control parameters (pH, cell growth and nutrients concentrations) were monitored.

Based on the results obtained from those trials, the photobioreactor designed by Greenskill was selected to be implemented at the Wastewater Development Centre of Scottish Water in Bo’ness, Scotland (Figure 4.1.9), as it appeared to be the most suitable for the growth of *Chlamydomonas acidophila*.

Figure 4.1.9: Greenskill Environmental Technology Ltd. 75L and 500L PBRs installed at the Wastewater Development Centre in Bo'ness (Picture: Greenskill Environmental Technology Ltd.)

4.1.3 Analyses of results of I4 operation

4.1.3.1 *I4 Demonstration unit trial in Bo'ness (75L PBR)*

The settled effluent after the primary treatment was selected for the trial in Bo'ness due to its higher NH_4 and COD concentrations (Table 4.1.1). The 75L PBR designed and manufactured by Greenskill Environmental Technology Ltd. was set-up on the 11th of March and settled effluent was fed semi-continuously for 4 months.

Figure 4.1.10: Greenskill Environmental Technology Ltd. 75L PBR implemented at the Wastewater Development Centre in Bo’ness (Picture: GCU)

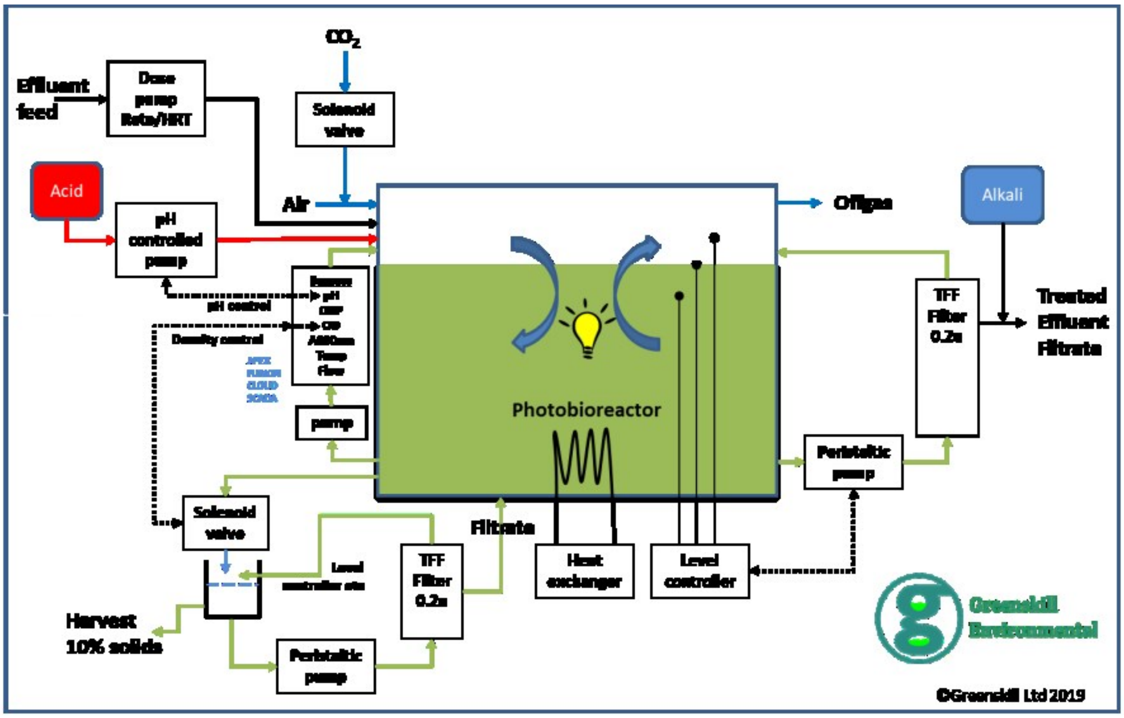


Figure 4.1.11: Treatment process configuration with 75L PBR (Picture: Greenskill Environmental Technology Ltd.)

The central unit was a 75L tank fed with settled effluent with an HRT of 3.75 days. The tank was continuously illuminated at a low rate of 0.4 Amp. The light is usually the limiting factor in microalgae technology, as it contributes to the higher energy consumption. However, *Chlamydomonas acidophila* have shown to require low light intensities and therefore, a low rate of 0.4 Amp was enough to achieve successful nutrients recoveries.

The temperature was kept between 22 to 24 °C using an external refrigerating cooler and submersible heater. CO_2 was supplied at the beginning of the trial to accelerate the start-up phase in the reactor, however, once the microalgae started growing, CO_2 supply was not required.

The microalgae biomass was retained in the PBR by a tangential flow filter, type-Microgon, MiniKros Tangential flow separation module with hollow fibre membrane (TFF) P/N: M22M-600-01N, Media: Methyl ester, Pore side: 0.2μm, Surface area: 6500cm^2. It was backwashed twice per day for 5 min. During the 4 month trial, it did not foam or exhibit biofilm formation neither in the Greenskill PBR nor in the filter, even though we were treating settled wastewater which contains more suspended solids than the final effluent. Therefore, it seems that tangential flow filter is a suitable option for retaining the cells in the reactor without getting blocked.

The biomass concentration started increasing in the PBR reaching values up to 2g L^{-1}. On the 21st of June (day 90 of trial), 75 % of the volume in the reactor was removed and inoculated into the 500L reactor. An increase of Optical density (OD) was observed due to the dilution of the culture (Figure 4.1.12), however, the microalgae cells grew exponentially in the following days, reaching a biomass concentration of 2g L^{-1} in just 4 days.

Figure 4.1.12: Changes in the optical density in 75L PBR from the 19th till the 25th of June 2019

The microalgae achieved promising nutrients recovery after a long period of acclimatization, reaching values of around 3-5 mg PO_4 L^{-1} d^{-1} and 8-10mg NH_4 L^{-1} d^{-1} (Figure 4.1.13) under very low light intensities.

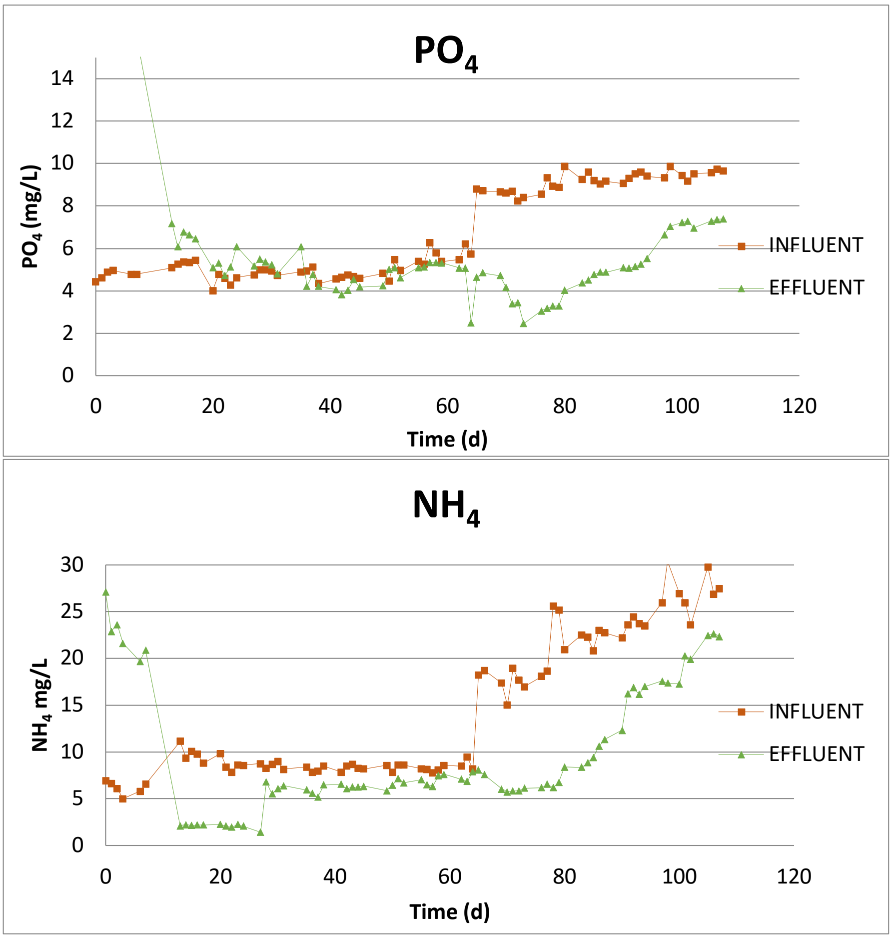


Figure 4.1.13: PO_4 and NH_4 concentrations in the influent, tank and effluent during the trial in Bo'ness (75L PBR)

Furthermore, this technology seems to remove around 50 % of the COD from the settled effluent (Figure 4.1.14), reaching values close to the ones reported in the final effluent after the secondary treatment (40 – 60 mg L^{-1}). Therefore, this technology appears to be promising as a secondary-tertiary treatment in wastewater treatment plant.

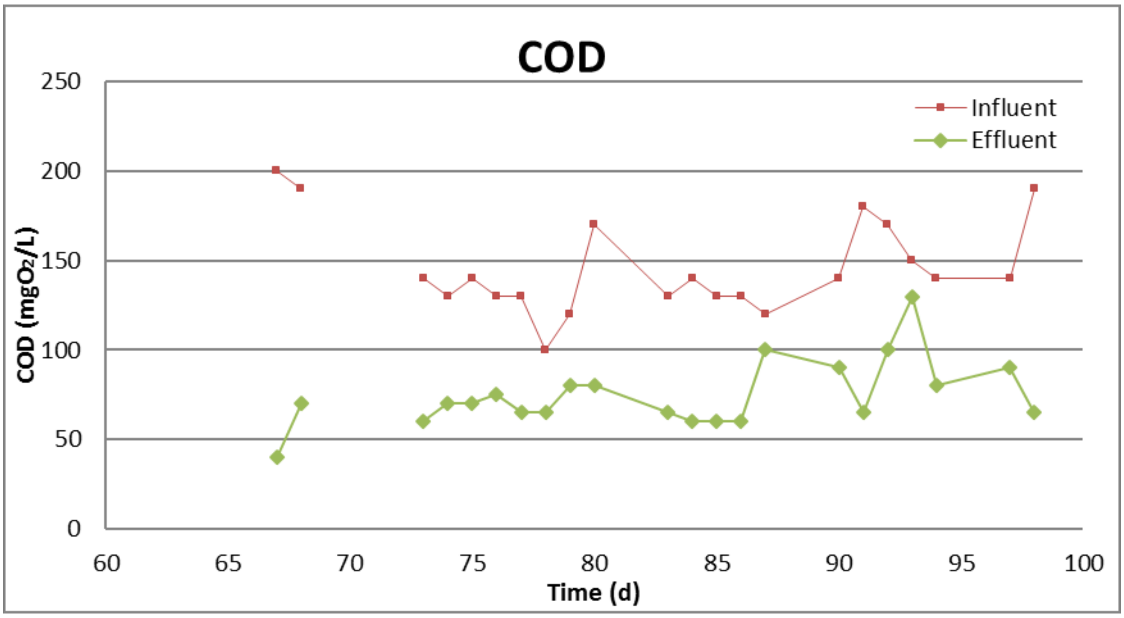


Figure 4.1.14: COD concentrations in the influent and effluent (75L PBR)

4.1.3.2 *Results of I4 Demonstration unit trial in Bo'ness (500L PBR)*

The settled effluent after the primary treatment was selected for the trial in Bo'ness due to its higher NH_4 and COD concentrations (Table 4.1.1) and the successful results obtained in the trial using the 75L PBR. The 500L PBR designed and manufactured by Greenskill Environmental Technology Ltd. was set-up on the 24th of June 2019 and settled effluent was fed semi-continuously.

Figure 4.1.15: Greenskill Environmental Technology Ltd. 500L PBR implemented at the Wastewater Development Centre in Bo'ness (Picture: GCU)

The central unit was a 500L tank fed with settled effluent with a HRT of 2 - 3.75 days. The tank was continuously illuminated at a low rate of 0.4 Amp. The light is usually the limiting factor in microalgae technology, as it contributes to the higher energy consumption. However, *Chlamydomonas acidophila* have shown to require low light intensities and therefore, a low rate of 0.4 Amp was enough to achieve successful nutrients recoveries.

The temperature was kept between 22 – 24 °C using an external refrigerating cooler and submersible heater. CO_2 was supplied after the 17th of September 2019 in order to improve the nutrients consumption.

The microalgae biomass was retained in the PBR by a tangential flow filter, type-Microgon, MiniKros Tangential flow separation module with hollow fibre membrane (TFF) P/N: M22M-600-01N, Media: Methyl ester, Pore side: 0.2µm, Surface area: 6500cm^2. It was backwashed twice per day for 5 min. During the trial, it did not foam or exhibit biofilm formation neither in the Greenskill PBR nor in the filter, even though we were treating settled wastewater which contains more suspended solids than the final effluent.

Therefore, it seems that tangential flow filter is a suitable option for retaining the cells in the reactor without getting blocked.

The biomass concentration started increasing in the PBR reaching values up to 4 g L^{-1} (Figure 4.1.16) and therefore, on the 24th of October 2019, 10 % of the reactor's biomass was harvested on a weekly basis. The microalgae biomass was settled by the addition of 0.5 g NaOH L^{-1}, in which the mixture reached a pH of 10 and therefore the microalgae formed flocs that were easily settling in around 5 minutes (Figure 4.1.16). This recycled P product was dried and stored for further quality assessment as part of WP T2 (around 1 kg of biomass was achieved by the end of December 2019).

Figure 4.1.16: On the left, microalgae biomass concentration in the PBR. On the right, microalgae biomass sedimentation after 5 min without (1) and after the addition of 0.5g L^{-1} of NaOH (2) (Picture: GCU)

The microalgae achieved promising nutrients recovery after a long period of acclimatization, reaching values of around 50 to 75 % of PO_4 and 75 to 100 % of NH_4 (Figure 4.1.17) under low light intensities.

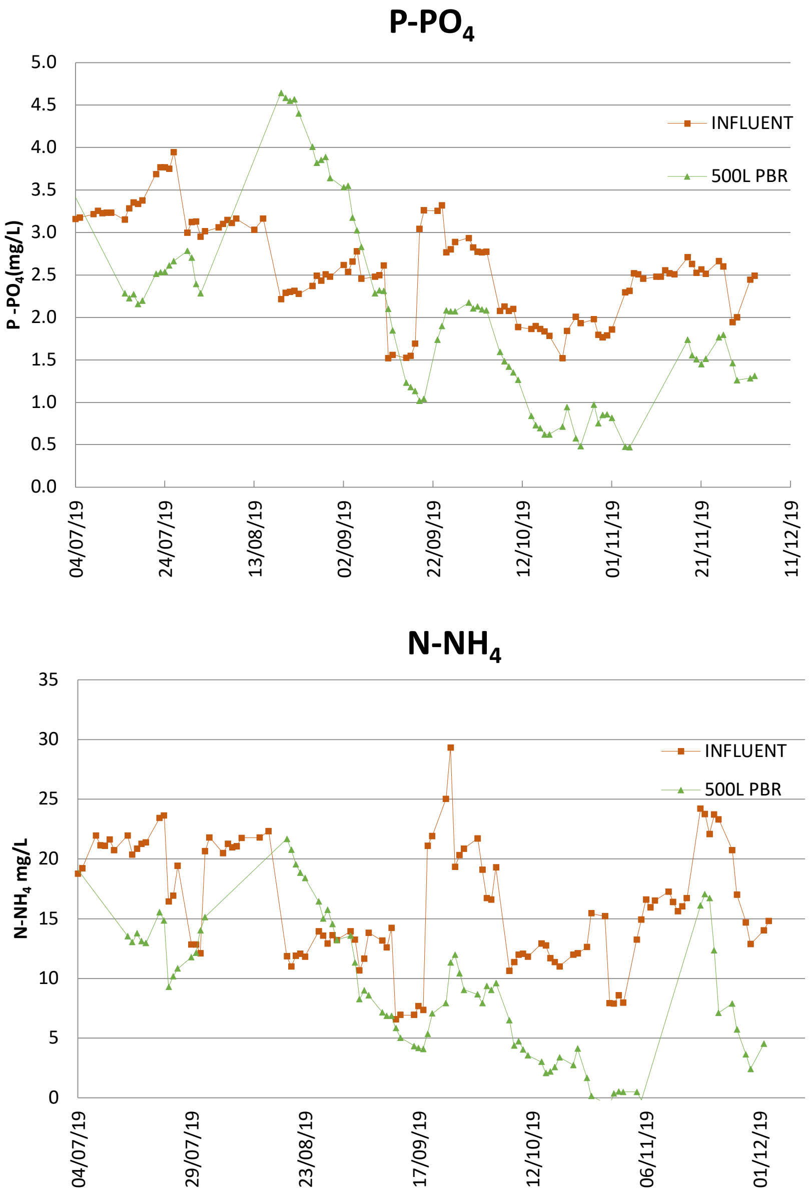


Figure 4.1.17: PO$_4$ and NH$_4$ concentrations in the influent, tank and effluent during the trial in Bo'ness (500L PBR)

Furthermore, in the scaling up of this technology to 500 L PBR, this system still removed around 50 % of the COD from the settled effluent (Figure 4.1.18), reaching values lower or close to the ones reported in the final effluent after the secondary treatment (40 – 60 mg L^{-1}). Therefore, this technology appears to be promising as a secondary-tertiary treatment in wastewater treatment plant.

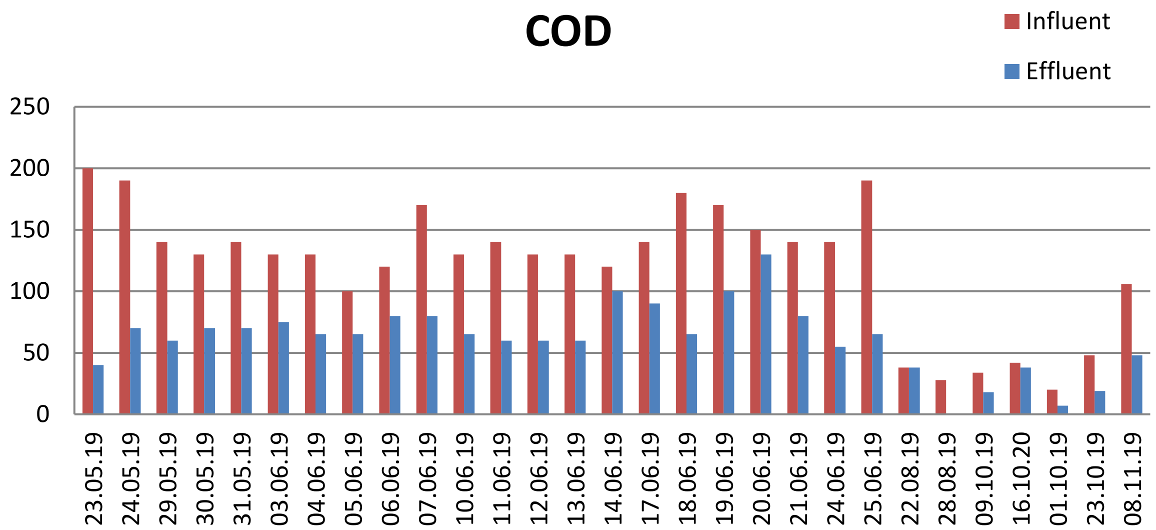


Figure 4.1.18: COD concentrations in the influent and effluent (500L PBR)

4.1.4 Discussion of results for I4 operation

Wastewater treatment plants are considered to be one of the biggest phosphorus polluters and, therefore, P discharge standards have been readjusted to reduce the nutrient input to meet the goals of the European Union Water Framework Directive, especially in sensitive areas (Scottish Environment Protection Agency (SEPA) 2014; European Parliament 2015).

As mentioned before, recovering P from small wastewater treatment plants faces several challenges as suitable systems require robustness and low maintenance plus the variability of P in wastewater is often high. Based on the results obtained in the 10 months trial in Bo'ness, *Chlamydomonas acidophila* microalgae technology seems to be suitable for these type of treatment plants as it has shown to be robust, it can be maintained long term as a mono-algal culture (without being invaded by other species, due to operation at low pH values) and it can recover P and N from wastewater with high variability of nutrients.

This extremophile microalgae *Chlamydomonas acidophila* has shown several advantages over other conventional microalgae used for recovering nutrients from wastewaters. The low pH in the media facilitated a long-term mono-algal culture without the invasion of other microorganisms, since most of the microorganisms present in wastewater do not survive in such an extreme pH environment. Furthermore, the microalgae did not foam or exhibit biofilm formation in the PBR during the 10 months of trial due to the continuously low pH, which is normally used in the cleaning of membrane filters. It was thus easy to separate biomass using tangential flow filtration, which is usually one of the limiting factors in microalgae technology.

Moreover, *C. acidophila* requires much lower light intensities and temperatures to grow and consume nutrients than other microalgae used for wastewater treatment, which leads to a lower energy consumption by the demonstration unit.

The onset of the Water Framework Directive across Europe required a reduction in P discharge levels below the current value of 1.2 mg L^{-1}, specified within the Urban Wastewater Treatment Directive to 0.5 mg L^{-1} (European Parliament 2015). *C. acidophila* has shown successful nutrient removal reaching values in the effluent of below 1-0.5 mg L^{-1}, indicating potential for the use in wastewater treatment.

Many studies use final effluent for the microalgae growth to avoid inhibition derived from high concentrations of NH_4 and COD in primary effluents and the competition with other organism present in the wastewater such as bacteria and fungi (Luo et al. 2017). However, *C. acidophila* have shown to be able to grow and consume nutrients in primary effluent and thus in the presence of high NH_4 concentrations and even reduce this compound's concentration by 80- 100 %. Moreover, since this microalga is mixotrophic, it removed around 50 % of the COD from the primary effluent, reaching values close to those reported for final effluent after conventional secondary treatment (40 – 60 mg L^{-1}). Therefore, this technology appears to be promising as a secondary-tertiary treatment in wastewater treatment plant.

The bioreactors used in these trials, like most of the current algal bioreactors, rely on suspended cultures. These culture systems often require a large amount of energy to harvest algal cells and eliminate water downstream – estimated to be up to 30 % of the costs (Gross et al. 2013; Molina Grima et al. 2003; Uduman et al. 2010). However, after addition of 0.5g L^{-1} of NaOH, *C. acidophila* forms flocs that settle in under 5 minutes, enabling easy harvesting and separation from the liquid phase.

The recovered microalgae biomass potential ranges from 1.3 to 2.6 Mg/y/plant, based on WWTP capacities of 100 PE – 200 PE, with an average P-content in the dry microalgae biomass of around 1.4 % (41-82 kg P_2O_5/y/plant), N-content of 7 %, and further main components such as plant hormones, vitamins, fatty acids and antioxidants. This biomass could be distributed locally in remote, rural and island locations. Low seasonal variability in quantity and quality can be expected, due to the low light intensity supplied and required by *C. acidophila* (Escudero et al. 2020b).

Recycling this microalgae biomass as a biofertiliser has the reported potential of enhancing soil fertility, plant growth, nutrients dynamic, fruit quality and nutritional characteristics and grain yield. Also, *C. acidophila* accumulates carotenoids, valuable antioxidants able to improve plant growth. In addition, the non-harmfulness of potential residual elements of the wastewater where *C. acidophila* grew are to be assessed. Such potential benefits and risks are further investigated in a work package of the Phos4You project, dealing with the quality assessment of recovered P materials.

4.1.5 Conclusion for I4

Most advanced wastewater treatment technologies are typically not feasible in rural WWTPs, since these small sites require simple, robust and affordable systems. Based on the results obtained in the 10 months' trials in Bo'ness, this microalgae technology seems to be suitable as a secondary/tertiary treatment of wastewater for these small sites. Since *Chlamydomonas acidophila* has shown to be robust (resistant to NH_4, COD and several pollutants' concentrations), it can be maintained long term as a mono-algal culture (due to its dominant nature under low pH values) and it can remove P, N and COD from wastewater under very low light intensities.

It is acknowledged that light availability is one of the greatest challenges for microalgae cultivation and therefore, *C. acidophila's* high photosynthetic efficiency is essential to decrease the costs of microalgal biomass production. Furthermore, it did not foam or exhibit biofilm formation in the PBR and it is easy to separate using tangential flow filtration, which is usually another key challenge in microalgae systems.

4.2 Demonstrator I5: P adsorption for small scale use (FILTRAFLO™-P with CCM adsorbent)

Authors: Szabolcs Papp, Mark Taggart, Barbara Bremner (ERI); Cédric Mébarki (Veolia)

Phosphorus (P) recovery (and potentially re-use) through adsorption has been identified as a promising technology as this involves low energy consumption, may provide various economic benefits, is simple technology to apply, and it may be highly effective even at low P concentrations. Recovery of P from wastewater through adsorption onto natural solid waste material may also provide a low-cost P-rich product that could be re-purposed (i.e., as a soil improver), provided the final material is also low in other co-adsorbed contaminants. If a P-saturated adsorbent can also be re-purposed in this way (i.e., used as a P-rich soil enhancer in agriculture), this would be highly consistent with the principles of a ‘circular economy’, whereby re-use or recycling of waste materials is optimised to extract maximum value (Zheng et al. 2019).

Crab carapace is composed mainly of calcium carbonate (calcite) and chitin, and is a common waste by-product from the seafood industry in Scotland and worldwide; with millions of tonnes created/wasted annually, most of which is disposed of in landfill (Lu et al. 2007). Re-purposing such waste into a value-added product, i.e., as a P-adsorbent and then potential soil enhancer, may provide multiple agricultural benefits including increasing soil organic matter content; improving soil physical properties (texture); provision of essential plant nutrients; and buffering (through $CaCO_3$ content) against soil acidification caused by nitrogen application. In addition, chitin/chitosan has antibacterial properties – which may in turn support rhizobial multiplication by biologically controlling root pathogenic organisms (Pap et al. 2020c).

As part of the Phos4You project, the Environmental Research Institute (ERI) has been developing a new adsorbent material from crab carapace and, together with Veolia, has been using the FILTRAFLO^{TM}-P Unit to recover P from wastewater treatment plant (WWTP) final effluent through a filtration/adsorption process. This small unit employs enhanced gravitational filtration through an adsorption media with continuous self-backwashing. Trials have been designed to assess how the FILTRAFLO^{TM}-P would operate under ‘real’ conditions, and to ascertain the effectiveness of the crab carapace-based chitosan-calcite material/adsorbent (CCM) to recover P from final effluent. Based on extensive lab-scale experiments, a six- week trial of this technology was carried out at the Scottish Water Horizons Development Centre at Bo'ness in January-February 2020.

4.2.1 Preparation of I5

4.2.1.1 *Adsorbent synthesis optimisation and characterisation*

Materials and methods

During the first stage of development, different seafood waste materials (oyster and mussel shells and crab carapace), were examined for their P adsorption capacity and characteristics. All raw materials were collected (as food waste) from a seafood restaurant in Scrabster, Scotland. In experiments, crab carapace showed the highest potential, based on its P adsorption capacity and physico-chemical structure. However, low P bonding potential indicated that further improvement of the crab carapace material was needed. Hence, a thermochemical activation process using potassium hydroxide (KOH) was utilised to produce a more effective P adsorbent (CCM). For adsorbent preparation, a response surface design (RSD) in conjunction with Box-Behnken design (BBD) process was used to optimise the synthesis technique. RSD and BBD determine the best connection between various effects/interactions and a group of variable parameters, leading to a better understanding of the minimum number of experimental runs needed to estimate the effect of those parameters, and identify optimal processing conditions.

During CCM optimisation, raw crab carapace was first mixed at different mass ratios with KOH, then placed into crucibles. These mixtures were placed into a muffle furnace and heated from room temperature up to different final temperatures, which were then held for varying times (see conditions below). After cooling, the resultant adsorbent samples were rinsed with Milli-Q water to eliminate any by-product residues, then dried at 105 °C for 2 h and stored in glass bottles. The final optimised adsorbent is referred to here as 'CCM'. The following preparation parameters were studied: (X1) impregnation ratio — IR (at 0.10 – 1.00 g of KOH per gram of material), (X2) activation time (30 – 180 min) and (X3) activation temperature (80 – 500 °C). These three parameters, together with their respective ranges, were chosen based on a literature review, ideal cost requirements and the outcomes of preliminary experiments. The optimised adsorbent was sieved to <250 μm (for batch experiments) and 0.5 – 2 mm (for column studies).

The percentage of P removal, R (%), and the equilibrium adsorption capacity, q_e (mg P/g), were determined using:

$$R\ (\%) = \frac{C_0 - C_e}{C_0} \cdot 100 \tag{1}$$

$$q_e = \frac{(C_0 - C_e)}{m} \cdot V \tag{2}$$

Where C_0 is the initial P concentration, C_e is the residual concentration (mg P/L), V is the volume of solution (L) and m is the mass of the CCM (g) used.

The surface structure and elemental composition of both the raw/untreated crab carapace and the final CCM adsorbent were determined using a Scanning electron microscope (SEM; Topcon SM-300) equipped with a Titan XPP analogue X-ray pulse processor (EDX). Textural characterisation was determined using nitrogen adsorption at 77 K using an Autosorb iQ instrument (Quantachrome, USA). Fourier transform infrared (FTIR) spectra (Perkin Elmer Spectrum) were collected over the range 500 – 4500 cm^{-1}. X-ray powder diffraction (XRPD) data were collected on a Bruker D2 Phaser diffractometer in reflection geometry, using Cu *Ka* over the two-theta range 6 – 60° for a total data collection time of 10 min. Samples were prepared as thin smears by grinding them in acetone and placing the resulting suspension on a silicon substrate.

Results and discussion

Figure 4.2.1a–d shows that for the conditions studied, removal of P increased with increasing IR. Figure 4.2.1e–f shows that the interaction between activation temperature and time has little/no significant influence on P adsorption. However, Figure 4.2.1a–d demonstrates that a longer activation time and a moderate activation temperature (in combination with IR) slightly enhances P adsorption efficiency. At an IR of 1.0, the greatest P adsorption was achieved. To achieve maximum effectiveness and reduce preparation costs (in particular, keeping energy/electricity usage low), the activation temperature for verification experiments was set between 80 and 105 °C. Activation temperature has the greatest impact on production cost but had the lowest impact on P removal efficiency. Other parameters were set as per the optimisation process.

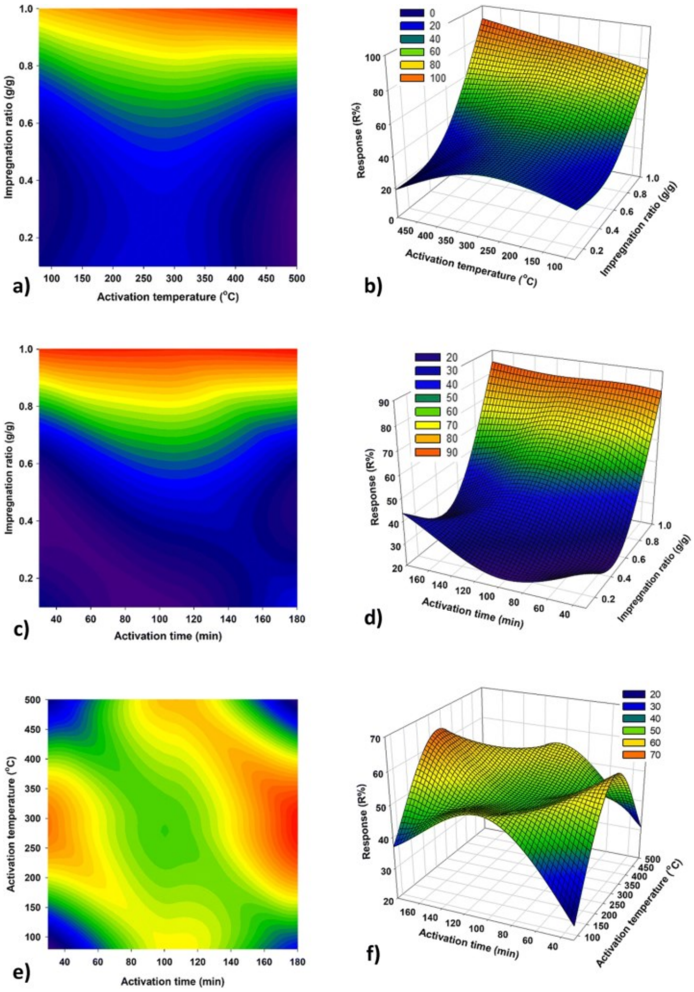


Figure 4.2.1: Contour and three-dimensional response surface plots regarding the effect of IR and activation temperature (a-b), IR and activation time (c-d) and activation temperature and activation time (e-f) on phosphorus adsorption (Pap et al. 2020a)

Within the set temperature range, the predicted optimal values were therefore as follows: X_1 = 1.0 g/g, X_2 = 105 °C, and X_3 = 150 min, to achieve maximum P removal of 75.89 %, with an overall desirability result of 0.964. The verification was then examined by running experiments using these conditions, and the removal efficiency obtained in this experiment was 78.11 %.

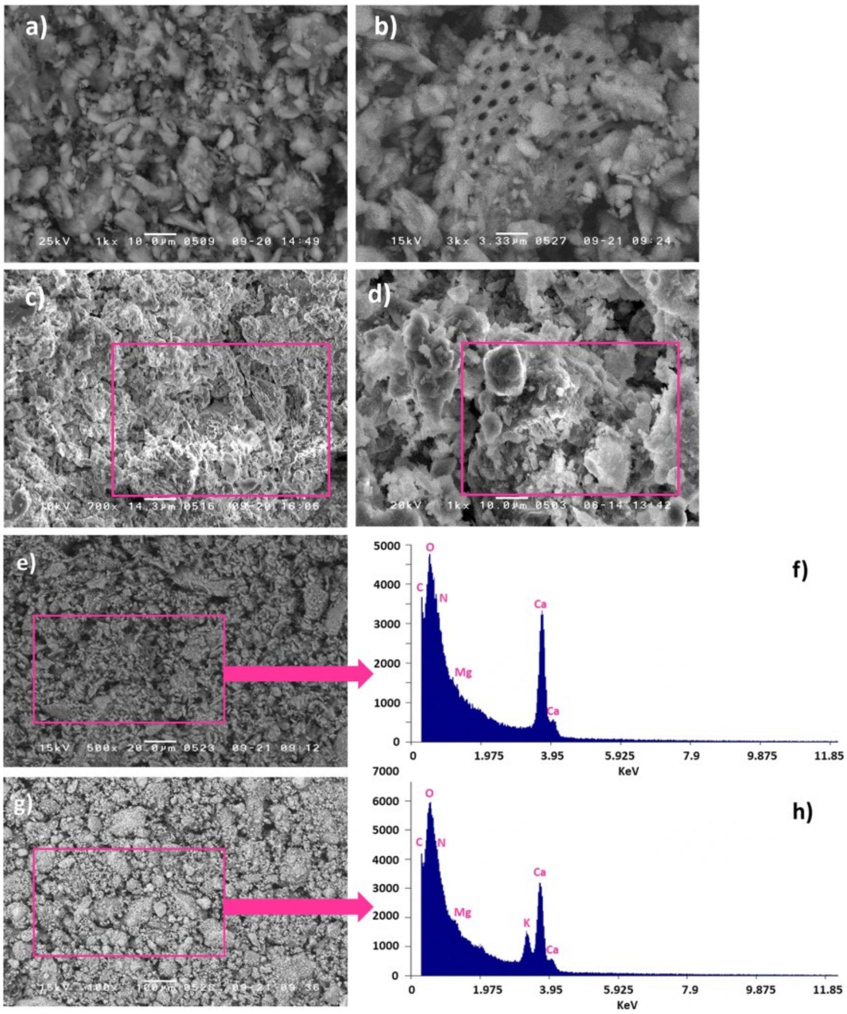
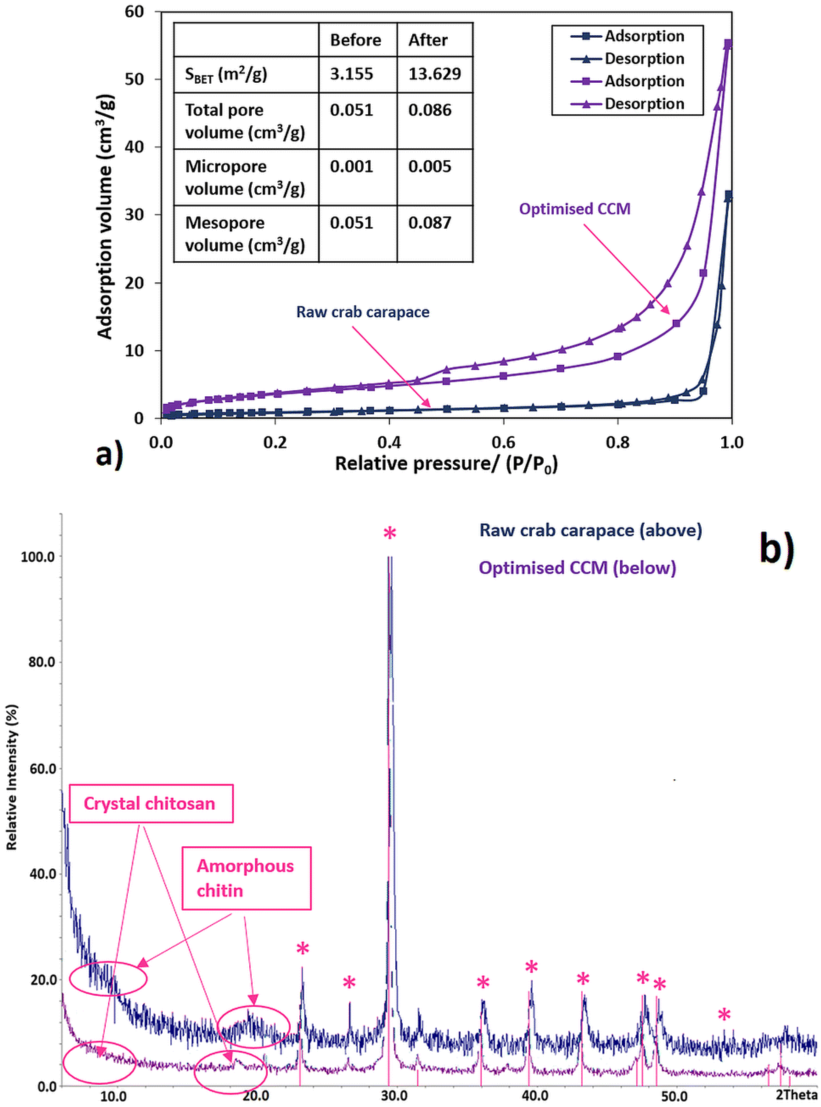


Figure 4.2.2: SEM micrographs of pristine crab carapace (bar lengths 10 μm and 3.33 μm; magnification × 1000 and × 3000) (a–b); optimised CCM adsorbent (bar lengths 14.3 μm and 10 μm; magnification × 700 and × 1000) (c–d); SEM micrographs with EDX spectra for pristine crab carapace (e–f); the optimised CCM adsorbent (note the additional potassium-K signal) (g–h) (Pap et al. 2020a)

In order to assess if the KOH alkaline treatment had an effect on the porosity and textural structure of the crab carapace, SEM micrographs of raw material (Figure 4.2.2a, b) and the optimised CCM adsorbent (Figure 4.2.2c, d) were taken. SEM micrographs reveal certain irregular surface morphology and features as well as some particle aggregation. From Figure 4.2.2c, d, it is obvious that the surface of the final CCM is rougher (compared to the raw material). The CCM also had various cracks on the surface which were attributed to the deformation effect of milling and activation. Cracks are randomly distributed over the CCM surface. The non-uniform distribution of cracks is due to the presence of the polymer.

Figure 4.2.2e–h further shows SEM-EDX spectra for the raw crab carapace and the final CCM material. The EDX spectrum of the material after the optimisation with KOH shows the characteristic peak for K, which confirms the presence of K alongside other elements (such as C, O, N, Mg and Ca), and shows KOH has impacted the process. The presence of all mono- and divalent ions on the CCM surface will assist in the formation of new Ca-P, Mg-P and K-P crystals. This surface precipitation phenomena is also generally favoured at alkaline pH.



	Before	After
S_{BET} (m^2/g)	3.155	13.629
Total pore volume (cm^3/g)	0.051	0.086
Micropore volume (cm^3/g)	0.001	0.005
Mesopore volume (cm^3/g)	0.051	0.087

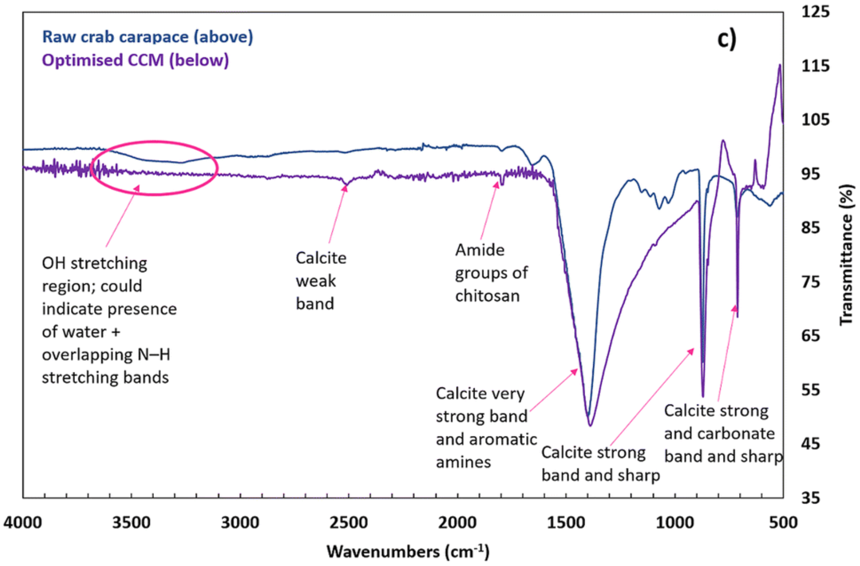


Figure 4.2.3: Nitrogen adsorption/desorption isotherms and BET data of raw crab carapace and the CCM adsorbent after optimisation (a), XRPD patterns of raw crab carapace and the optimised CCM adsorbent (Note: * reflections associated with calcite) (b) and FTIR spectra of raw crab carapace and the optimised CCM adsorbent (c) (experimental conditions: impregnation ratio for KOH:carapace (g/g) 1:1; activation temperature 105 °C; activation time 150 min) (Pap et al. 2020a)

N_2 adsorption/desorption isotherms are widely used to determine the surface area and porosity of adsorbents. The N_2 isotherm data for the raw carapace material and CCM material are shown in Figure 4.2.3a, which exhibits a type IV isotherm with a H4 hysteresis loop (IUPAC classification) at $P/P_0 = 0.995$. This clearly indicates that both materials are mesoporous in nature. N_2 adsorption in the region of $P/P_0 < 0.1$ for the CCM further indicates the coexistence of micropores. The S_{BET} surface area, total pore volume, micropore volume and mesopore volume of the two materials are summarised in Figure 4.2.3a. The specific surface area for the crab carapace (before activation) was 3.155 m^2/g, which increased markedly (>4 fold) to 13.629 m^2/g post-activation. Likewise, total pore volume increased from 0.051 to 0.086 cm^3/g.

The raw and activated materials were also characterised by XRPD (Figure 4.2.3b) to identify the phase(s) present in each sample. The normalised XRPD patterns show the presence of both an amorphous phase - which is associated with the organic component of the material, e.g., the chitin/chitosan polymer; and a crystalline phase - which was identified as calcite. In order to explore surface functionality, FTIR spectra were recorded (Figure 4.2.3c). The most obvious functional groups on the surface were: hydroxyl, amide and calcite groups (more information can be found in Pap et al. (2020a).

4.2.1.2 *Bench-scale Phosphorus (P) adsorption optimisation on the Chitosan-Calcium Adsorbent (CCM)*

Materials and methods

Batch and dynamic lab trials using different experimental conditions were undertaken to optimise P removal efficiency by the CCM and determine the governing removal mechanisms. To assess the effect of pH on P adsorption, 200 mg of CCM was added to 50 mL of P solution (at 20 mg/L P) in Erlenmeyer flasks. The pH of solutions was adjusted within the range of 2.0 – 12.0 with 0.1 M HCl or NaOH. Flasks were then placed on an orbital shaker (IKA KS 260) at 150 rpm for 120 min at room temperature (22 °C).

Adsorption kinetics (influence of contact time) were investigated using 500 mg of CCM in 500 mL of P solution (20 mg P/L) at two different temperatures (22 and 42 °C). Solution pH was not adjusted (but had a starting pH of ~7), and the Erlenmeyer flasks were shaken at 150 rpm. Samples were taken over a 300 min contact period, at predetermined time intervals (1, 5, 15, 30, 45, 60, 90, 120, 180, 240 and 300 min).

Adsorption isotherms (influence of equilibrium concentration) were created at three different temperatures (22, 32 and 42 °C) using 100 mL solutions containing different initial P concentrations (within the range of 1–50 mg P/L), with a CCM dose of 100 mg.

P desorption experiments were conducted by first adding 100 mg of CCM into 50 mL of 50 mg/L P solution, then shaking for 2 h. The resultant P-loaded CCM was then separated from the suspension by centrifugation at 4000 rpm for 10 min. The P-loaded CCM was then desorbed using 3 different solutions separately (a) 2 % citric acid, (b) 0.5M HCl, and (c) Milli-Q water – using a liquid/solid ratio of 500 mL/g (i.e., 0.1 g in 50 mL of eluent) at 22 °C. After a 2 h contact time, eluent supernatants were removed and measured for P concentration. At the same time, blank experiments were carried out to quantify the 'background' P dissolved from the primary (unloaded) CCM adsorbent.

Dynamic column studies were conducted at room temperature using glass columns (20 cm length, 2 cm internal diameter). Glass wool was placed at the bottom and top of the column to prevent adsorbent washout. P working solutions were continuously fed in an up-flow mode into the column by peristaltic pump (Masterflex, Cole-Parmer Instrument Co., USA). The influent contained different P concentrations (5, 10, and 20 mg P/L) and passed through varying column bed-heights (3, 6 and 10 cm) using three flow rates (3.5, 7.0, and 10.5 mL/min). Samples were collected at regular time intervals (using an ISCO Foxy Junior fraction collector) to obtain breakthrough curves. The breakthrough time (t_b) was taken when the outlet P concentration attained 10 % of the inlet concentration, whilst the exhaustion time (t_e) was determined when the effluent P level reached 90 % of the inlet concentration. The maximum column capacity, q_{total} (mg) for a given set of conditions was calculated from the area under the plot for the adsorbed P concentration, C_{ad} (mg P/L), versus time, as given by:

$$q_{total} = \frac{QA}{1000} = \frac{Q}{1000}\int_{t=0}^{t=t_{total}} C_{ad}dt \tag{3}$$

Where $C_{ad} = C_i - C_e$ (mg/L), t_{total} is the total flow time (min), Q is the flow rate (mL/min) and A is the area under the breakthrough curve (cm^2).

The equilibrium uptake (q_{eq}), i.e., the amount of P adsorbed (mg) per unit dry weight of adsorbent (mg P/g) in the column, was given by the equation:

$$q_{\mathrm{eq}} = \frac{q_{\mathrm{total}}}{W} \tag{4}$$

Where W is the total amount of adsorbent (g) in the column.

Results and discussion

The influence of initial P concentration on P adsorption onto the CCM was investigated within a concentration range from 1.0 to 50 mg P/L, at three different temperatures. As shown in Figure 4.2.4a, P adsorption capacity gradually increased as the initial P concentration and temperature increased. Maximum adsorption capacities were 21.56, 23.88 and 24.85 mg P/g at 22, 32 and 42 °C, respectively. Further, P adsorption behaviour was explored using two isotherm models (Langmuir and Freundlich) and the curves at different operating temperatures are provided in Figure 4.2.4a. The good Langmuir isotherm fit, implies that the adsorption of P onto the CCM relates to monolayer adsorption. This may be because modification of the CCM (with KOH) increased surface homogeneity, creating a finite number of binding sites for P adsorption.

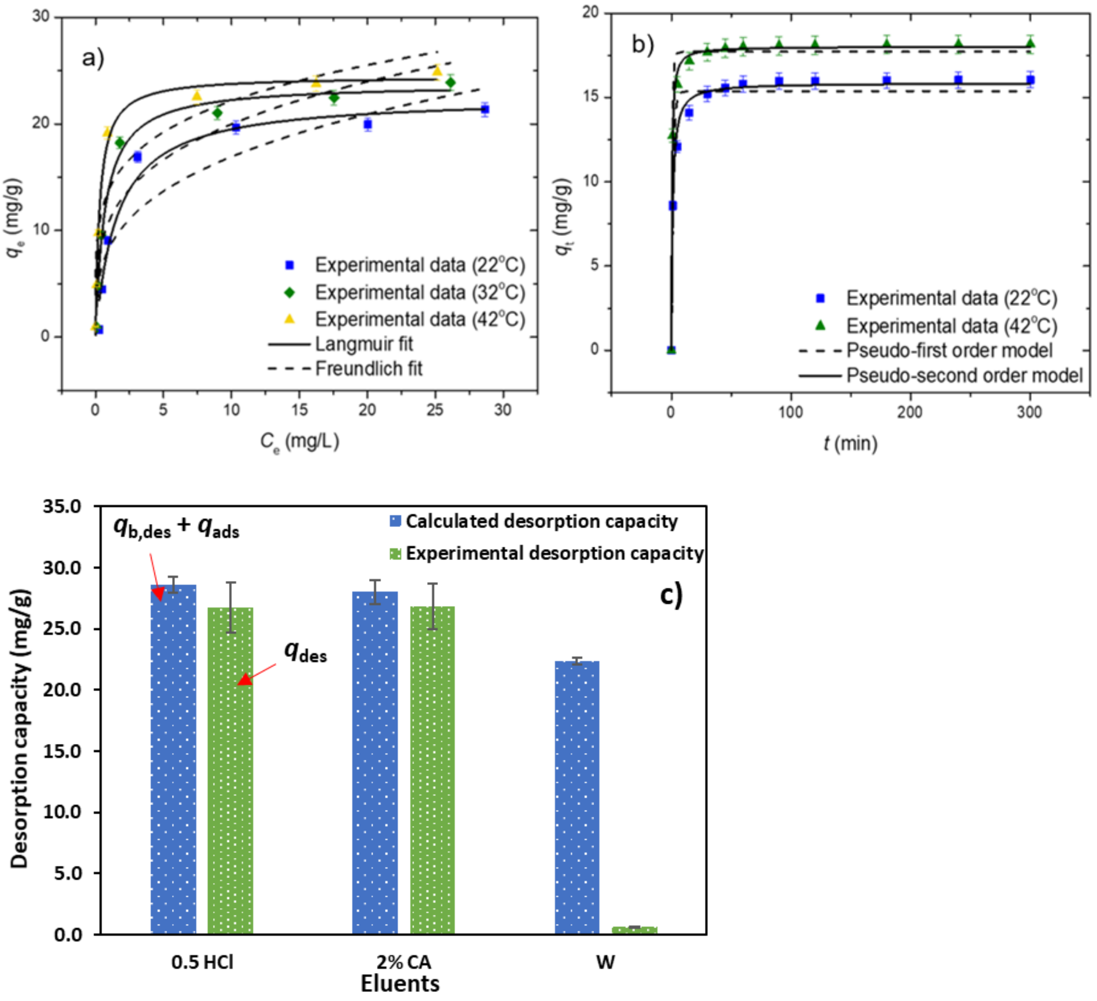


Figure 4.2.4: Batch adsorption experimental results: adsorption equilibrium data (a), adsorption reaction kinetics (b) and P desorption in water, using 0.5 M HCl and 2 % citric acid as eluents (c) (initial concentration: 1–50 mg P/L; no pH adjustment; contact time: 1-300 min; dose of adsorbent: 1 g/L; rotation speed: 150 rpm - Note: the data (n = 3) are represented as mean ± standard error); (Pap et al. 2020b)

Adsorption kinetics consider the rate of adsorption and help define likely reaction/mass-transfer mechanisms. As shown in Figure 4.2.4b, rapid adsorption is observed in the first 5 minutes, then adsorption slows. The CCM-P system reached equilibrium after ~120 mins (Figure 4.2.4b). In addition, higher temperatures (22 → 42°C) had a positive influence on P removal. The initial rapid adsorption suggested that P removal was initially controlled by outer-sphere surface complexation (electrostatic attraction). Numerous vacant adsorption sites (i.e., protonated OH and NH_2), and rapid diffusion (driven by the concentration gradient between the liquid/solid interface) will cause this rapid adsorption. Subsequently, adsorption slowed as other mechanisms, e.g., inner-sphere complexation (ligand exchange) and micro-precipitation began to be more dominant processes. These kinetic experimental results were fitted to pseudo-first order

(PFO) and pseudo-second order (PSO) reaction models. The best fit with the PSO model indicated that the adsorption of P onto CCM was chemisorption-dominated.

Figure 4.2.4c further shows the results of the P desorption experiments. The total potential 'calculated desorption capacity' was the sum of P desorption from unloaded samples ($q_{b,des}$) and the P adsorption capacity of the CCM (q_{ads}). These were 28.61, 28.00 and 22.35 mg P/g for 0.5 M HCl, 2 % citric acid and water, respectively. The experimental desorption capacities using the P loaded CCM were 26.74, 26.84 and 0.62 mg P/g, respectively. As such, only the water extraction was ineffective at removing the bound P (a potential 'benefit' in an agricultural soil application setting, where rapid release of P would be undesirable).

Figure 4.2.5a shows the adsorption performance of the CCM with various bed heights (3, 6, 10 cm), at a constant flow rate (7 mL/min) and inlet P concentration (10 mg P/L). Breakthrough time (t_b) increases from 0 to 305 min, while exhaustion time (t_e) increases from 530 to 845 min when the bed height increases from 3 to 10 cm. P adsorption capacity was also enhanced, with q_{eq} = 1.4 up to 2.2 mg P/g. Greater bed height increased the total number of binding sites and solute residence time, allowing P to more efficiently/effectively adsorb onto the CCM. A greater bed height also allowed a longer contact time between the adsorbent and adsorbate (1.3–4.5 min).

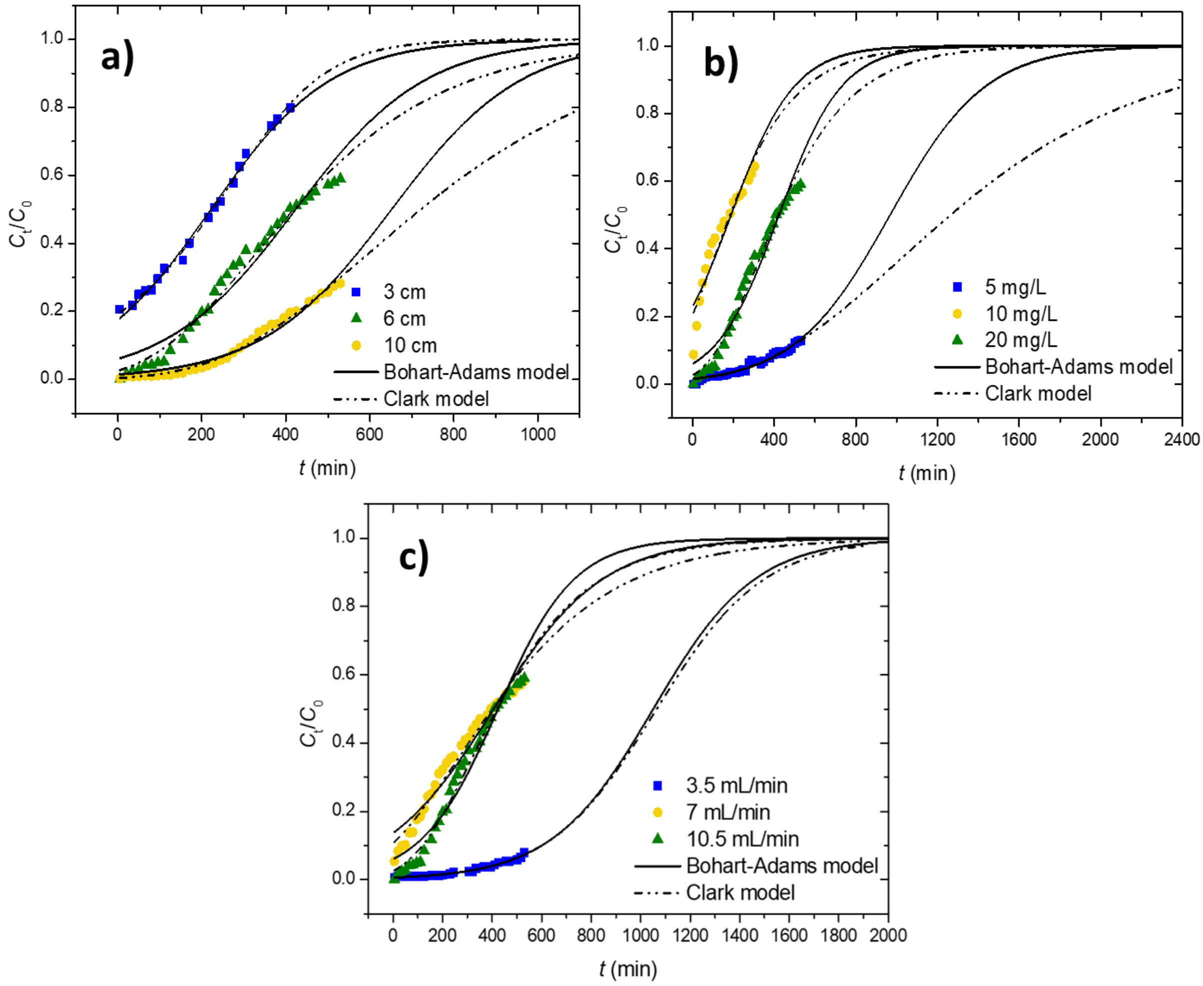


Figure 4.2.5: Fixed-bed column adsorption experiments: effect of bed height (a), initial phosphate concentration (b) and flow rate (c) (initial concentration: 5-20 mg P/L; no pH adjustment; flow rate: 3.5-10.5 mL/min; bed height: 3-10 cm) ; (Pap et al. 2020b)

The effect of initial P concentration (5, 10 and 20 mg P/L) on P removal performance was studied at a fixed CCM bed depth (6 cm) and flow rate (7 mL/min). As shown in Figure 4.2.5b, the breakthrough curve becomes steeper as inlet P concentration increases. Further, the breakthrough time decreases (t_b = 485 to 0 min). Exhaustion time also declined with a rise in initial P concentration, from 1265 min (5 mg P/L) to 545 min (20 mg P/L) and q_{eq} (equilibrium uptake) decreased from 2.4 to 1.9 mg P/g as the inlet P concentration increased (Table 4.2.1).

The effect of flow rate (3.5, 7.0, and 10.5 mL/min) on P adsorption was investigated with a constant bed height (6 cm) and initial P concentration of 10 mg/L. As Figure 4.2.5c illustrates, breakthrough time (t_b = 620 to 50 min) and exhaustion time (t_e = 1550 to 845 min) reduced with increasing flow rate. The maximum capacity of the column decreased with increased flow rate (q_{eq} = 2.3 to 2.0 mg P/g), as shown in Table 4.2.1. At a higher flowrate, as the external film mass-resistance at the surface of the adsorbent tended to decrease, the residence time, and thus the saturation time also decreased, resulting in lower removal efficiency.

Adsorption modelling for breakthrough curves is necessary to gain insights into the relationships between column parameters. To predict the breakthrough curves obtained from experimental data as a function of time, two different mathematical models (namely Bohart-Adams and Clark models) were applied. Among the various breakthrough models commonly used, these two models can be considered as more refined as both involve mass-transfer and surface reaction concepts. It is evident that the experimental breakthrough curves for P (at different column operating conditions) were well predicted by both models over the entire period (more information can be found in Pap et al. (2020b).

Table 4.2.1: Varying operation conditions (bed height, flow and initial P concentration) and the results obtained for the fixed bed column experiments

Condition No.	***H* (cm)**	***Q* (mL/min)**	**C_0 (mg P/L)**	**t_b (min)**	**t_e (min)**	**V_{eff} (mL)**	**q_{total} (mg)**	**q_{eq} (mg/g)**
1	3	7	10	-	530	5600	10.9	1.4
2	6			155	710	7700	27.6	2.2
3	10			305	845	7700	42.6	2.2
4	6	7	5	485	1265	16100	30.5	2.4
5			10	155	710	7700	27.6	2.2
6			20	-	545	6230	25.8	1.9
7	6	3.5	10	620	1550	9993	28.8	2.3
8		7		155	710	7700	27.6	2.2
9		10.5		50	845	10500	25.4	2.0

4.2.2 Execution of I5

Based on the laboratory bench-scale results, the Veolia Water Technologies FILTRAFLO^{TM}-P pilot reactor was tested using the CCM adsorbent at the Scottish Water Horizons Development Centre at Bo’ness in January-February 2020 (Figure 4.2.6). The centre is situated next to/within the Bo’ness Wastewater Treatment Works, a fully operational WWTP that routinely employs advanced biological treatment to remove P (amongst other target variables) from wastewater. The Development Centre facilitates the application of pilot scale plant to the treatment of wastewater from the adjacent

WWTP that can be siphoned off (as required) from various stages within the WWTP (i.e., allowing trials using influent wastewater, primary/secondary or final effluents).

Figure 4.2.6: Scottish Water Horizons Development Centre at Bo'ness (Picture: Scottish Water Horizons)

A 100-L FILTRAFLO^{TM}-P pilot reactor, 1.2m in height and 0.5m in diameter, made from 0.5cm thick plastic was mounted on a wooden support housing box (Figure 4.2.7). FILTRAFLO^{TM}-P employs enhanced gravitational filtration through a granular media (here, the developed CCM) with continuous self-backwashing. The lower part of the reactor, shaped as an inverted circular cone (15 L in size; and ~30° slope angle), was designed to increase backwash efficiency (Figure 4.2.7a). The CCM granular adsorbent is shown in Figure 4.2.7b. The reactor is equipped with an air supported self-backwashing system on the bottom to enable adsorbent recirculation (Figure 4.2.7c). Through this system, the adsorbent from the bottom of the vessel can be airlift assisted (using an entrained compressed air flow) and reintroduced into the top of the reactor. As well as increasing adsorption efficiency, the backwashing helps to avoid compaction/biofouling of the granular media.

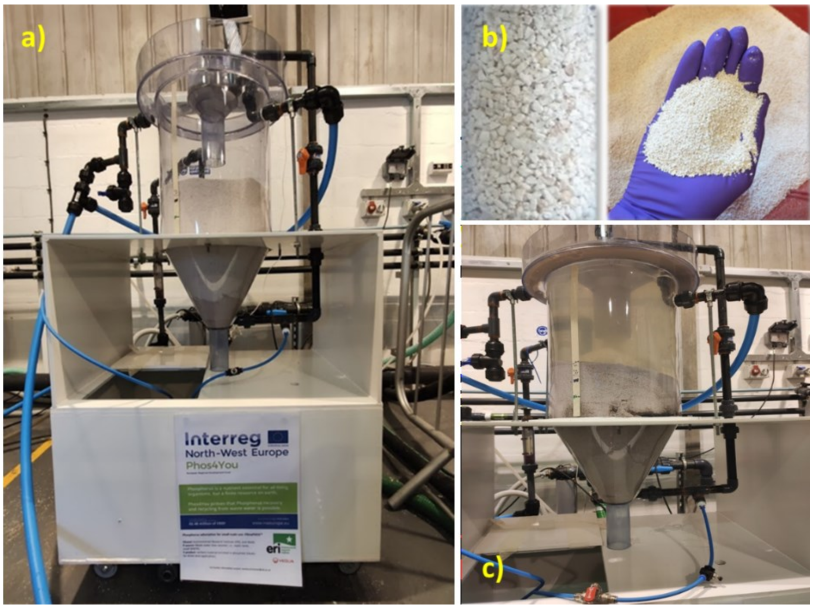


Figure 4.2.7: FILTRAFLO^{TM}-P pilot reactor designed by Veolia (a), the CCM adsorbent developed by ERI (b) and the airlift supported self-backwashing system visible at the bottom and right side of the unit (c) (Picture: ERI)

Several trial runs were conducted. During the first trial (#1), the reactor column was filled up to 15 cm bed depth (measured only from the base of the cylindrical part) with the CCM granules (~11 kg) of particle size 0.5 – 2 mm. These conditions were selected following the preliminary lab-experiments (to maximise P adsorption capacity and efficiency). Subsequently, for trials #2-4, the column was filled up to a 20 cm bed depth (Figure 4.2.8a) with the CCM granules (~15 kg). The reactor inlet valve, which was fitted to the middle of the reactor (Figure 4.2.8a), was connected with an accordion hose to feed inlet water (secondary treated wastewater) into the reactor. This was supplied from an intermediate 1 m^3 IBC tank (Figure 4.2.8b). The inlet water was diffused downward into the middle of the adsorbent bed volume (Figure 4.2.9). Another hose was connected to the outlet at the top of the reactor, to evacuate the filtered/treated water to a collection sewer (Figure 4.2.9). All valves were manually operated when needed.

The use of secondary wastewater effluent (without residual suspended solids) limited fouling of the adsorption bed. From the IBC tank, the wastewater was pumped into the adsorption bed at 200 L/h. An MXV electric submersible pump (Caprari) was used to convey water at the desired flowrate. For each run, once the adsorption bed was saturated (with P), the P loaded material was evacuated from the reactor manually and replaced with fresh adsorbent. The point at which saturation occurred was established using measurements of P using a Total Phosphate Tube Test (Lovibond™ Reagent Set) – by regularly measuring (every 2 hours) the inlet/outlet P concentration. The saturated

CCM was stored on site in plastic boxes until the end of the trial period. Subsequently, at the ERI laboratories, the saturated CCM was dried at 105 ºC overnight prior to further quality analysis. In total, four trials (#1-4) were conducted, two using low P concentrations (~1 mg P/L) and two with higher P concentrations (spiked to ~7 mg P/L within the IBC inlet tank). The other process parameters (such as the flowrate, adsorbent mass/bed height, etc.) were kept fixed during the trials (except for slight variation in trial #1 - see details above).

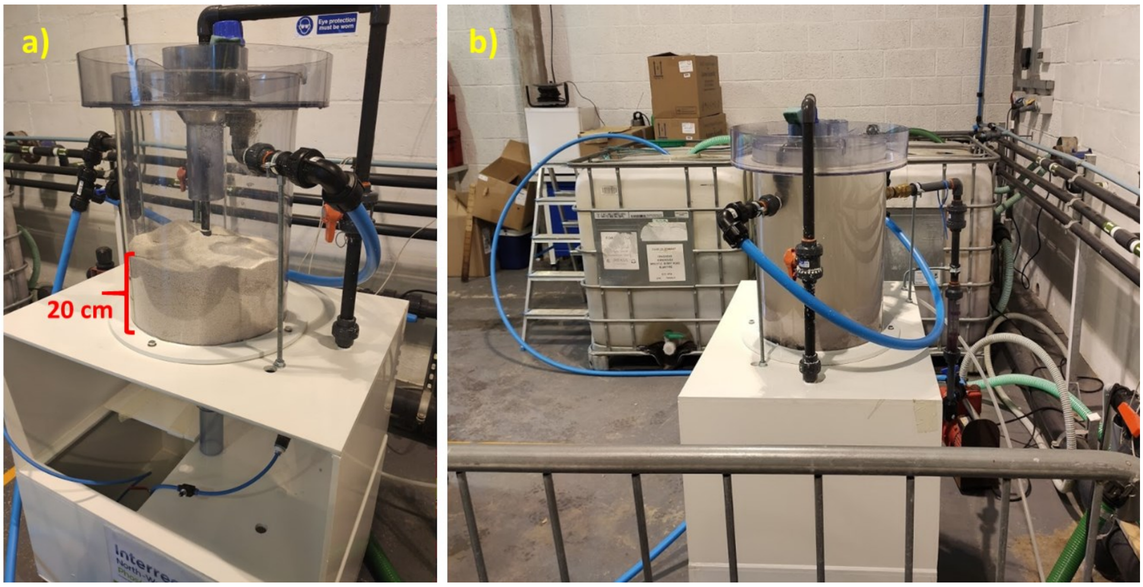


Figure 4.2.8: FILTRAFLO^{TM}-P pilot reactor valve system (a) and with the IBC tanks (b) (Picture ERI)

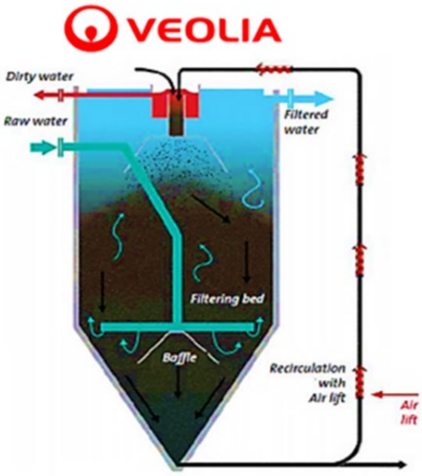


Figure 4.2.9: Wastewater circulation within the FILTRAFLO^{TM}-P pilot reactor (Source: Veolia)

Below, Figure 4.2.10 shows the schematic of the pilot test process. The secondary effluent from the Bo'ness WWTP was first pumped to an IBC tank, and then through the FILTRAFLO^{TM}-P pilot reactor filled with CCM adsorbent, and then filtered water was returned to the WWTP through the collection sewer which was located inside the test centre.

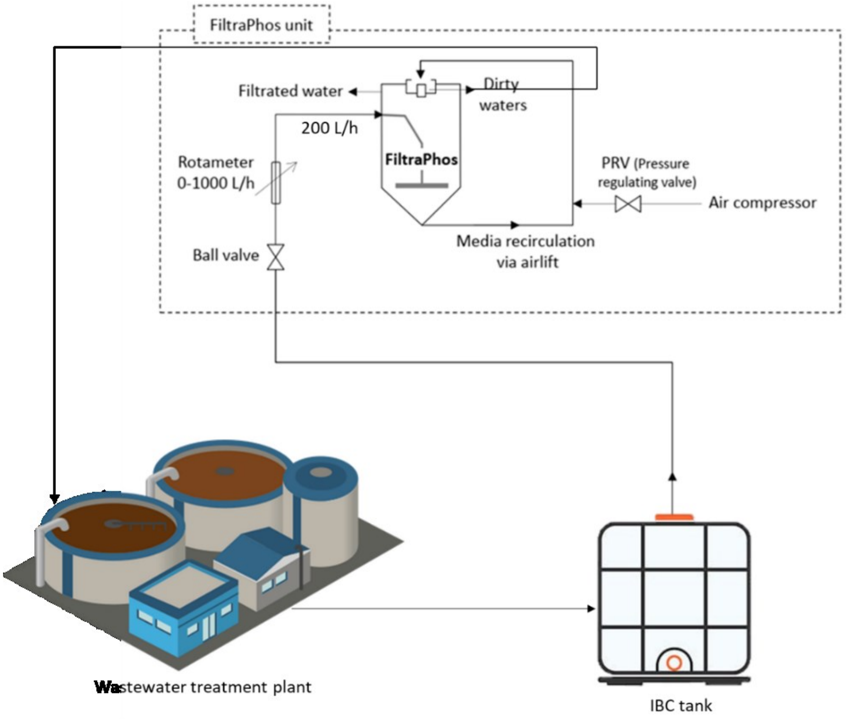


Figure 4.2.10: Schematic of the pilot test process run with FILTRAFLO™-P unit and CCM adsorbent

The typical composition of the secondary wastewater effluent used in the trials is shown in Table 4.2.2. Inlet/outlet samples (of about 1 L) were taken from the reactor every 2 h while running, and pH, conductivity, turbidity, P and COD were determined in the field immediately after sampling. Aliquots of each sample were also filtered through 0.45-µm pore-size nylon syringe filters (Fisher Scientific, UK) for further analysis using a Seal AQ2 Discrete Analyser, Shimadzu dissolved organic carbon (DOC) analyser and Varian inductively coupled plasma optical emission spectrometer (ICP-OES). The aliquot for ICP analysis was also stabilised/acidified with ultra-trace metal grade concentrated nitric acid (HNO_3) immediately following filtration. P concentrations obtained on site using the Total Phosphate Tube Tests were only used to track the P adsorption process in the field. These results were only considered indicative and were not standardised, therefore, they are not included in this report.

Residual phosphate, ammonium and TON (total oxidised nitrogen – nitrite + nitrate) concentrations were measured at the ERI labs using a SEAL AQ2 Discrete Analyser (Seal Analytical, UK). ICP-OES (Varian 720-ES) was used to determine dissolved P and metal concentrations in wastewater effluent samples. Instruments were calibrated within their linear ranges (all correlation coefficients >0.98); blanks and external standards were used to ensure quality control. DOC was analysed by high temperature catalytic combustion using a Shimadzu TOC-L instrument. The pH and conductivity of unfiltered samples were determined with a hand-held probe (HANNA HI991300 portable meter). This was calibrated for conductivity with a 1413 µS/cm standard solution, and for pH with certified pH 4, 7 and 10 solutions. Turbidity of raw samples was analysed using a HACH 2100Qis portable turbidimeter, calibrated with certified reference materials (CRMs 10, 20, 200 and 800 NTU). COD was analysed through the reactor digestion method using a DR890 Hach colorimeter.

Four trials (#1–4) were carried out at the WWTP between January 6th and February 7th, 2020. The 1 m^3 IBC inlet tank was filled with secondary wastewater effluent twice every day. As the flowrate was 200 L/h, one filtration 'run' took 5 h, with approximately 10 h per day run time.

Table 4.2.2: Typical composition of the secondary wastewater effluent used to test the FILTRAFLO™-P unit with CCM adsorbent

Parameters	Unit	Low concentration P trials		High concentration P trials	
		Trial #1	Trial #2	Trial #3	Trial #4
		Mean (±STDV)	Mean (±STDV)	Mean (±STDV)	Mean (±STDV)
pH	-	7.32 (±0.22)	7.38 (±0.30)	7.24 (±0.06)	7.37 (±0.34)
Cond.	*(μS/cm)*	1446 (±366)	1597 (±666)	1081 (±93)	1602 (±747)
Turb.	*NTU*	5.71 (±2.75)	15.00 (±21.90)	9.78 (±3.23)	6.55 (±2.88)
COD	*(mg/L)*	23.29 (±12.65)	26.00 (±5.39)	33.00 (±7.78)	38.45 (±8.66)
DOC	*(mg/L)*	4.64 (±2.03)	6.01 (±0.57)	5.18 (±0.66)	5.26 (±0.24)
$N\text{-}NH_3$	*(mg N/L)*	0.07 (±0.08)	0.02 (±0.02)	0.17 (±0.19)	0.52 (±0.55)
TON	*(mg N/L)*	8.07 (±2.28)	9.01 (±1.71)	8.18 (±1.71)	7.23 (±0.85)
Diss. P	*(mg P/L)*	1.32 (±0.10)	1.02 (±0.14)	7.14 (±0.49)	7.07 (±0.32)
SO_4^{2-}	*(mg/L)*	129.11 (±28.58)	190.38 (±23.63)	219.11 (±29.80)	101.80 (±18.60)
Diss. Al	*(μg/L)*	21.67 (±1.28)	22.40 (±1.72)	21.75 (±2.47)	23.78 (±3.55)
Diss. As	*(μg/L)*	<LOD	<LOD	<LOD	<LOD
Diss. Ca	*(mg/L)*	63.91 (±10.17)	78.29 (±7.46)	81.27 (±8.68)	63.20 (±10.45)
Diss. Cd	*(μg/L)*	<LOD	<LOD	<LOD	<LOD
Diss. Cr	*(μg/L)*	<LOD	<LOD	<LOD	<LOD
Diss. Cu	*(μg/L)*	1.30 (±0.24)	1.47 (±0.38)	1.32 (±0.35)	1.58 (±0.48)
Diss. Fe	*(μg/L)*	38.77 (±5.12)	42.36 (±5.24)	42.38 (±7.22)	35.86 (±4.43)
Diss. K	*(mg/L)*	12.52 (±2.59)	21.77 (±5.13)	30.69 (±4.81)	16.63 (±1.52)
Diss. Mg	*(mg/L)*	44.36 (±9.93)	70.86 (±11.13)	79.21 (±11.55)	33.42 (±6.29)
Diss. Mn	*(μg/L)*	21.18 (±20.58)	60.23 (±37.74)	84.71 (±57.9)	37.15 (±28.99)
Diss. Na	*(mg/L)*	167.52 (±57.74)	348.19 (±123.86)	372.69 (±108.9)	120.50 (±56.67)
Diss. Ni	*(μg/L)*	2.34 (±0.81)	2.19 (±0.70)	2.38 (±0.73)	1.98 (±0.58)
Diss. Pb	*(μg/L)*	<LOD	<LOD	<LOD	<LOD
Diss. Zn	*(μg/L)*	11.56 (±2.00)	12.89 (±2.02)	11.88 (±2.09)	12.18 (±1.78)

4.2.3 Analyses of results of I5 operation

Figure 4.2.11a and b gives the C_e/C_i vs time (h) data and the theoretical breakthrough curves of P during each trial with the CCM. C_e/C_i is the relationship between effluent (C_e) and influent (C_i) P concentration.

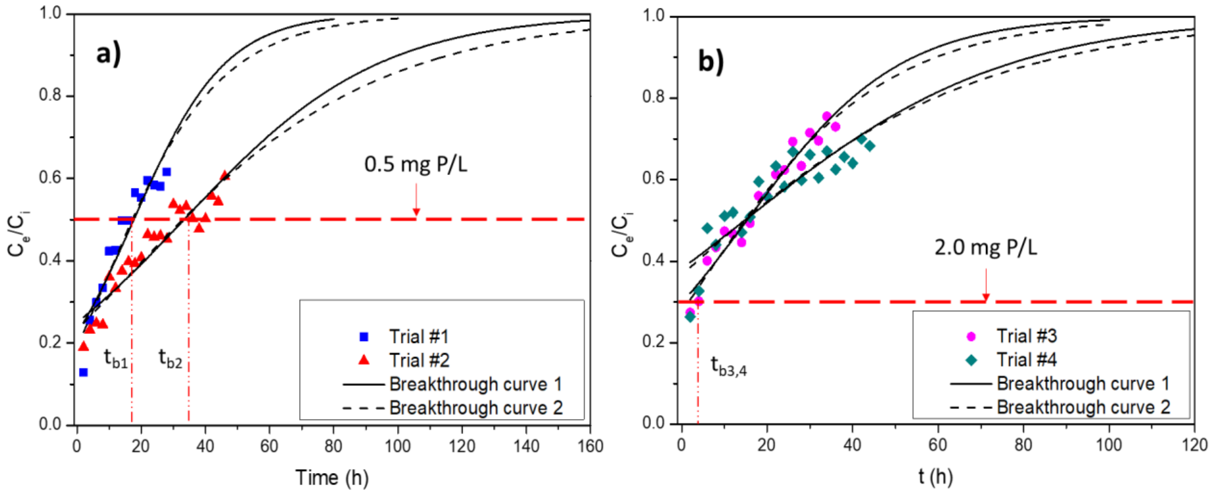


Figure 4.2.11: P theoretical breakthrough curves (Bohart-Adams with solid line; Clark with dash line) for the field trials. Low P concentration influents (a) and high concentration influents (b) (0.5 mg P/L being the EU Water Framework Directive (WFD) and US National Pollution Discharge Elimination System (NPDES) regulation limit for sensitive water bodies and the 2 mg P/L point the common effluent limit EU member states need to meet depending on population equivalence and the presence of sensitive areas)

The points on the curve (from measurements) initially describe the saturation process/trend over time, how the packed bed column becomes saturated over time (saturation at C_e/C_0=1). The shape of the curves indicates that breakthrough occurred significantly faster at higher P inlet concentrations. The breakthrough curve became steeper as the P concentration increased from 1 mg P/L to 7 mg P/L. Breakthrough times (shown as t_b) were calculated for the points at which (a) the outlet P concentration attained 0.5 mg P/L for the low concentration P trials (0.5 mg P/L being the EU Water Framework Directive (WFD) and US National Pollution Discharge Elimination System (NPDES) regulation limit for sensitive water bodies), and (b) the 2 mg P/L point for the high P trials (the common effluent limit EU member states need to meet (often either 1 or 2 mg P/L) depending on population equivalence and the presence of sensitive areas). The t_{b1} and t_{b2} values were 17 h and 35 h, while the $t_{b3,4}$ was 4 h (Figure 4.2.11a and b, respectively). The breakthrough time decreased with increasing influent P concentration, however, as expected, adsorption capacity increased with increasing influent P concentration. The adsorption capacity increased approximately five-fold, from 300 mg/kg and 363 mg/kg (trial #1 and #2) to 1590 mg/kg and 1859 mg/kg (trial #3 and

#4). The obvious difference in P adsorption pattern between trial #1 and #2 could be explained as different CCM masses were used in the FILTRAFLO^{TM}-P reactor in these 2 trials (~11 kg vs ~15 kg). The overall P-recovery rate of the demonstrator during the trials was 60 %.

The ratio of effluent and influent pH (C_e/C_i) is shown in Figure 4.2.12a. The initial pH of the wastewater influent was generally neutral and during the process the pH increased to ≈8.5, which indicates the alkali nature of the CCM (pH_{pzc} = 8.78). Since the process did not drastically alter the pH of the treated effluent (to extremely basic or alkaline), it would not be necessary to regulate outlet water pH after a 'real' water treatment scenario - thus reducing the need for additional chemicals/reagents (and reducing operational costs).

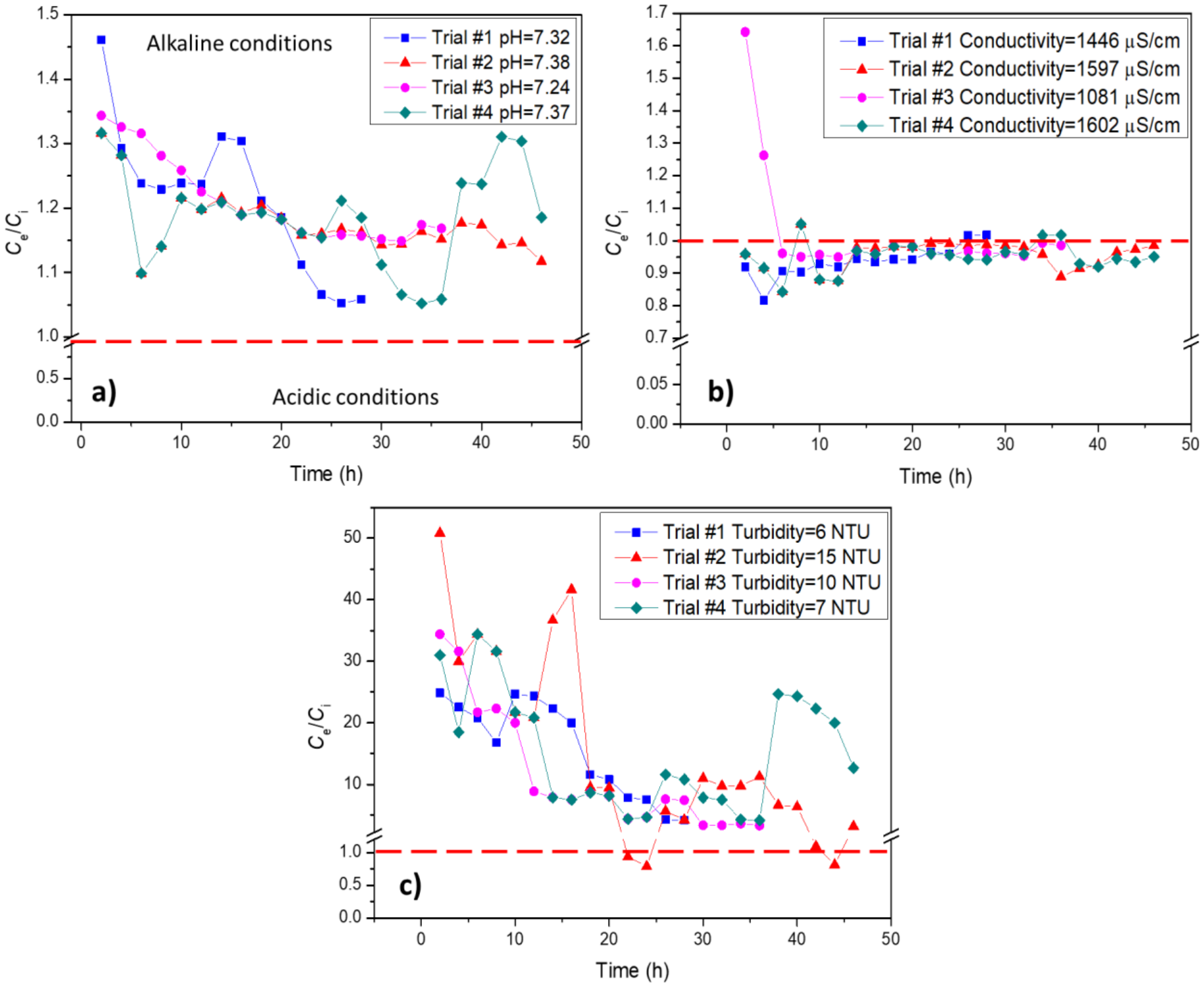


Figure 4.2.12: The ratio between effluent and influent levels (C_e/C_i) for pH (a), conductivity (b) and turbidity (c) during the trials

Similarly, in CCM treated water the conductivity reduced slightly (Figure 4.2.12b), while the turbidity increased during the trials (Figure 4.2.12c) (see Discussion).

To determine the potential to remove other nutrients beyond P (e.g., sulfate, TON (Total Oxidised Nitrogen), ammonium) and organic matter (expressed as chemical oxygen demand, COD and dissolved organic carbon, DOC), these were also measured before and after the trials (Figure 4.2.13a-d). Additionally, various macro- (Mg, Ca, K, Na) and micro-elements (Al, Fe, Cu, Mn, Ni, Zn) were monitored (Figure 4.2.14a-d). Results revealed that DOC, Mg, Ni, and K were released into the effluent, while COD (during trial #1 and #2) and ammonium (during trial #1) were also released. Ca, Cu, Fe, Mn and Zn were removed. The concentration profiles for other parameters largely remained unchanged or only varied slightly during the trials.

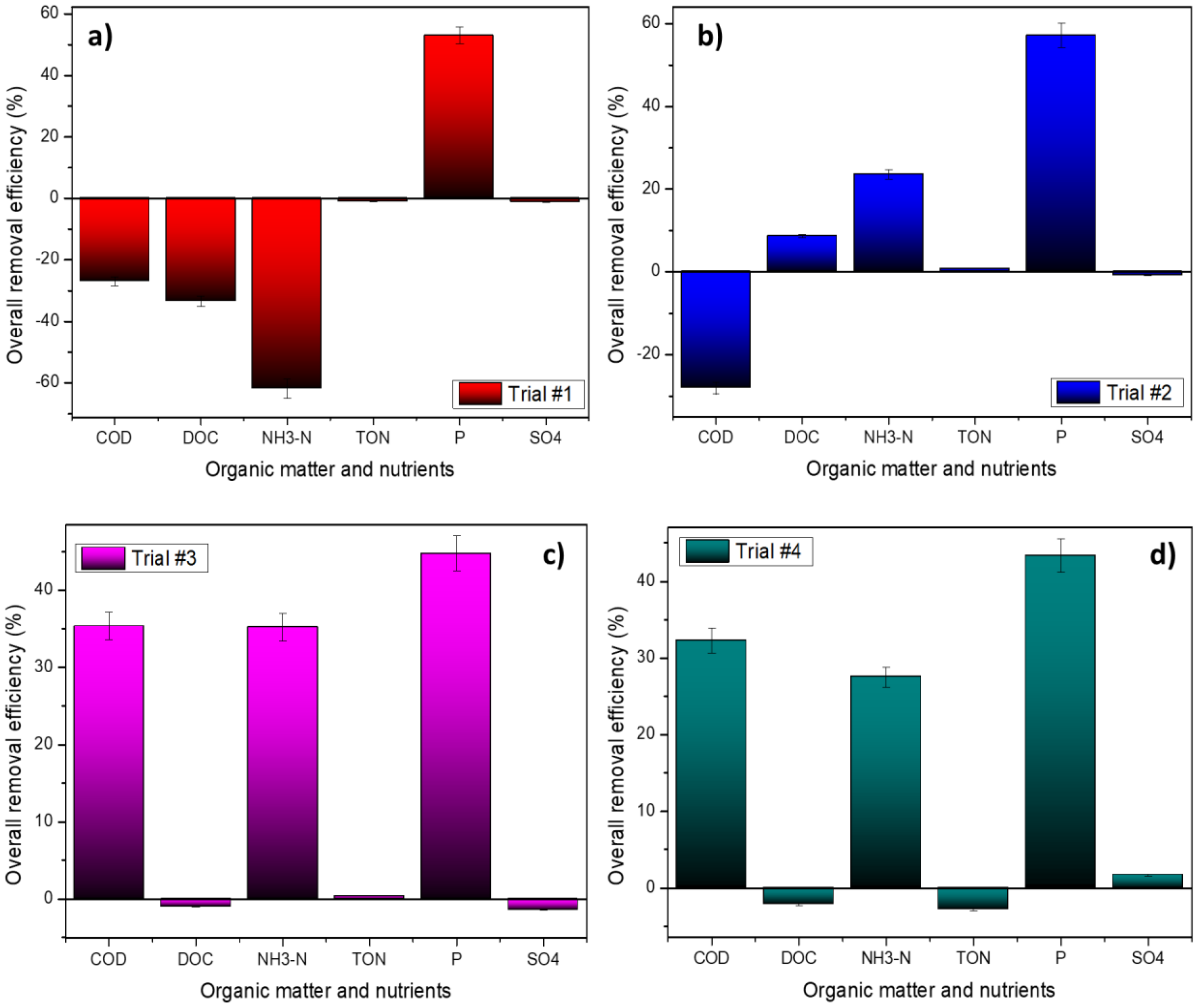


Figure 4.2.13: Organic compound and nutrient removal efficiency during the trials (a-d)

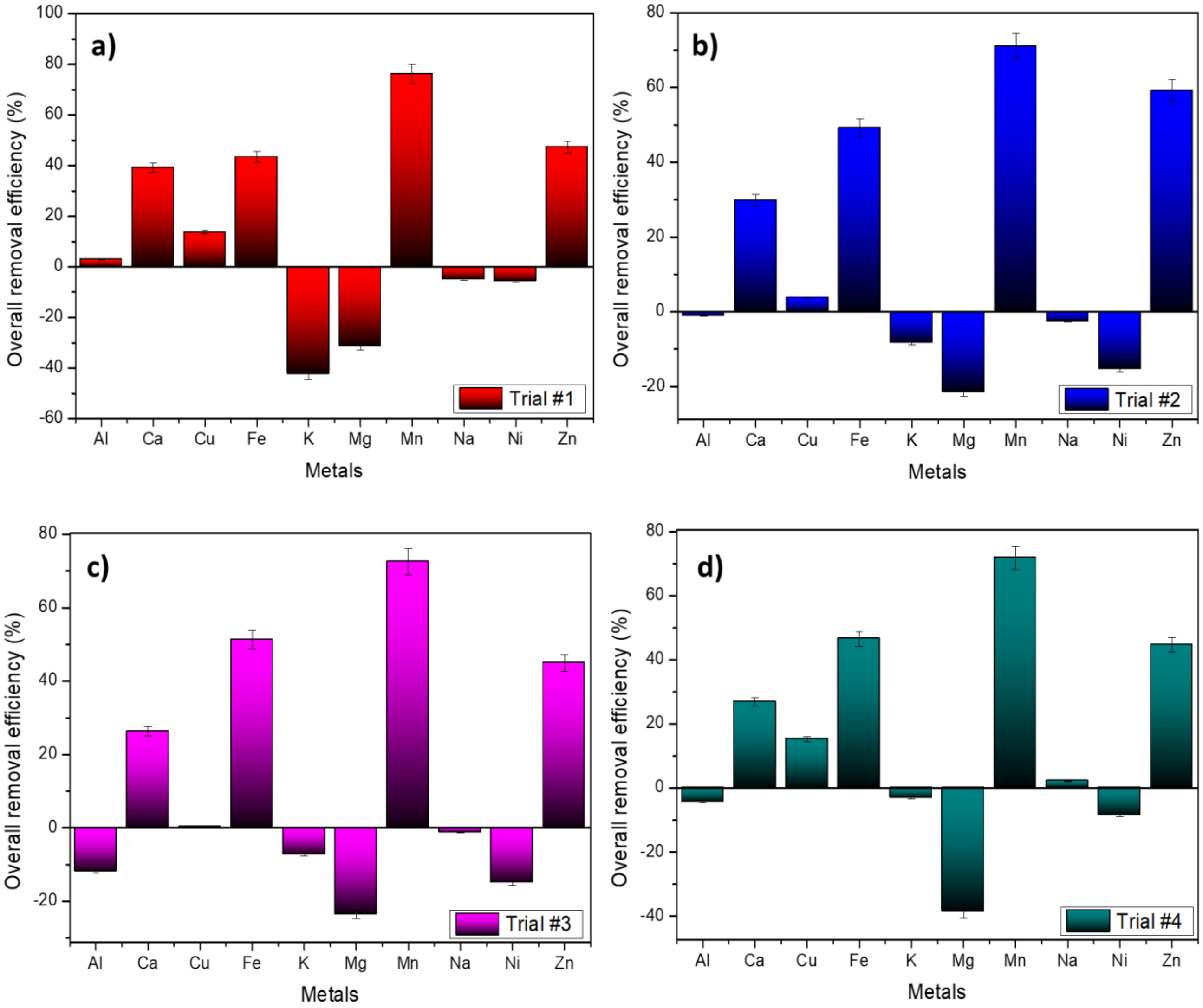


Figure 4.2.14: Macro- and micro-element removal efficiency during the trials (a-d)

4.2.4 Discussion of results for I5 operation

The results from the P adsorption trials indicated two quite different options for the FILTRAFLO^{TM}-P reactor combined with the CCM adsorbent. As Figure 4.2.11a illustrates, the CCM adsorbent was capable of removing P even at low concentrations, bringing residual P levels below 0.5 mg P/L. This shows its applicability in terms of polishing low-P effluents (i.e., its potential for use in preventing eutrophication in sensitive receiving waters). Further, the high P concentration trials showed its high P harvesting potential. From the theoretical breakthrough curves on Figure 4.2.11b it can be estimated that with 15 kg of CCM approximately 20 m^3 of wastewater could be filtered (whilst harvesting P). Further process optimisation should be considered, related to the bed height in the reactor, flow rate of the influent and granulation of the CCM adsorbent.

At alkaline pH values, OH^- ions may interfere directly with P adsorption; but this may be (partially) counteracted by favoured hydroxyapatite ($Ca_5(PO_4)_3(OH)$) precipitation on the CCM surface at pH 8–9 (a microprecipitation mechanism). Another important removal mechanism under these conditions was ligand exchange whereby $H_2PO_4^-$ and HPO_4^{2-} anions replaced CO_3^{2-} on the CCM surface and formed inner-sphere surface complexes (via Lewis acid-base interactions between P and $\equiv Ca–CO_3$ groups). P anions behave like Lewis bases, and can act as electron donors, donating electron pairs by binding to Ca atoms. At the same time, carbonate ions may be displaced into solution, driving pH increases (Figure 4.2.12a).

The sharp increase in turbidity at the beginning of each trial could be due to smaller/lighter adsorbent particles being washed out (flowrates were ~200 L/h). After this initial stage, the turbidity levels started to decrease again and stabilised at ~10 times the influent values (~50-60 NTU). This could be connected with the main CCM P removal mechanism, namely, the replacement of carbonate (CO_3^{2-}) ions. These may then form salts with available Mg, Na and K in the treated wastewater and thus increase turbidity. This points to the necessity to integrate/combine the FILTRAFLO^{TM}-P unit with further filtration (e.g., slow sand filtration). Slow sand filtration is a cost-effective and low energy technology. It easily integrates with physico-chemical (FILTRAFLO^{TM}-P) and biological processes for turbidity removal from wastewater (Verma et al. 2017).

CCM COD (indicative of organic compounds) and ammonium removal may have additional benefits, if this were to increase the organic carbon and nitrogen content of the loaded CCM material, assuming these organics are not undesirable harmful contaminants (which will be assessed/detailed in the Quality Examination report). Mg and K release could be explained by the material composition, since the CCM adsorbent contains high levels of Mg (originating from the crab carapace itself) and K (from the activation with potassium hydroxide).

Additional confirmation of the governing removal mechanisms at play for P, could be seen in the removal trends for metals such Ca, Cu, Fe, Mn and Zn. It is well known that alkaline earth and transition metals can strongly adsorb to phosphate between pH 6 and 9. They can thus bond to phosphate ions at the adsorbent surface through inner sphere complexation (e.g., ligand exchange with carbonates in this case).

4.2.5 Conclusion for I5

On the basis of above, the main conclusions here are:

- The optimum conditions found for the CCM adsorbent production process were a 1:1 ratio of potassium hydroxide: crab carapace (g/g), with an activation temperature of 105 °C and an activation time of 150 min.
- The produced CCM possessed higher crystallisation, richer surface chemistry, a larger surface area and higher porosity when compared to raw crab carapace.
- Lab-scale studies confirmed P to be effectively adsorbed onto the CCM under slightly alkaline conditions (pH > 7) through mixed mechanisms, which included mainly inner-sphere complexation (ligand exchange) and microprecipitation (as hydroxyapatite).
- The P-loaded CCM was also amenable to efficient desorption (using 0.5 M HCl or 2 % citric acid), indicating its potential to serve as P rich soil amendment material (wherein the P would not be excessively soluble, i.e., in water alone).
- High P removal/recovery potential was achieved in pilot scale WWTP trials even at low P concentrations, bringing the residual P level below 1 mg/L (the EU limit for sensitive water bodies).
- Surface microprecipitation and inner-sphere complexation were postulated as key P adsorption mechanisms in real wastewater effluent trials due to reduced concentrations of Fe, Ca, Cu, Mn and Ca. Also, the high inorganic carbon (carbonate) concentration in treated effluent indicated ligand-exchange through these metals (mainly Ca).
- The slightly increased turbidity noted in treated water (e.g., likely due to magnesium and potassium carbonates) may require integration/combination of the FILTRAFLO™-P unit with slow sand filtration.
- The results showed that the FILTRAFLO™-P unit with CCM could serve as a water polishing unit (with low P concentration effluents) and/or as a P harvesting unit (where P concentrations were high).
- Future work will involve pot and field-based plant growth trials to consider P uptake/availability in different soils/crops using the P-loaded CCM (using material obtained from the Bo’ness trials or from other trials in the future on different P rich waste streams).

4.3 Demonstrator I6.2: P precipitation at small-scale WWTPs (downscaled Struvia™)

Authors: Joe Harrington, Denise Barnett, Niamh Power, Asif Siddiqui, Ciaran O´Donnell (MTU); Cédric Mébarki (Veolia)

The demonstrator I6.2 aims to investigate the process of phosphorus removal and its recovery from municipal wastewater using lime for chemical precipitation; this is one of a range of P-recovery technologies from wastewater that has been applied (Bunce et al. 2018; Cornel and Schaum 2009; Macintosh et al. 2019; Ryan et al. 2016).

4.3.1 Preparation of I6.2

Background

A vital element of the investigation is the operation of a pilot plant at an Irish municipal wastewater treatment plant. A trial agreement to operate a pilot plant at the Macroom Wastewater Treatment Plant (WWTP) was developed and formally signed on 26th September 2019 between Munster Technological University (MTU) and Irish Water. This was preceded by a comprehensive study of potentially suitable wastewater treatment facilities in the Cork Region before the Macroom Plant was selected for the pilot study. In compliance with the agreement, all relevant MTU staff members have completed the necessary training (Safe Pass and Manual Handling) and have undertaken the necessary course of vaccinations to meet the Irish Water requirements to work at the WWTP. Following the Covid-19 pandemic (March 2020) additional health and safety documentation and actions were required to protect the public, MTU and Irish Water staff and for general operations at the Macroom WWTP. A comprehensive Covid19 health and safety risk assessment and plan was prepared in line with public health guidance. The items implemented for the health and safety plan included procedures for travel to and from site, and onsite procedures for PPE, social distancing and sanitization.

The pilot plant is based on the Struvia™ technology (developed by Veolia Water, France - Veolia Water Technologies 2016) and is located at the Macroom Wastewater Treatment Plant. The Macroom wastewater treatment plant (WWTP) was selected as a suitable site for the Struvia™ P-Recovery pilot plant after an extensive search commencing in September 2017. The WWTP is located approximately 35 km west of Cork city. It represents a typical Irish WWTP in terms of population served, influent type, treatment processes etc. The plant has a design load of 5,230 PE, which is typical of many Irish WWTPs with PE ranges of 2,000 to 10,000.

Macroom WWTP

The WWTP process outlined in Figure 4.3.1 comprises of an extended aeration activated sludge plant with preliminary treatment, sludge thickening and dewatering. The inlet channel contains a high-level storm overflow prior to an automated rotary screen. This screen removes rags and suspended objects from the wastewater. The material is washed and compacted before disposal to a skip. The rotating screen is bypassed in times of higher flow, and flow passes through a manually cleaned grate. All flows which go forward to full treatment are screened to 6 mm. Flows are then measured in the open channel venturi flume before gravitating into the activated sludge system comprising an oxidation ditch with a settling tank and a return sludge system. The oxidation ditch is a carousel type aeration tank with a capacity of 1240 m^3 and a high hydraulic retention time (HRT). This ditch was previously fitted with two horizontal shaft surface aerators. However, one of these was replaced with two 7.5 kW submerged venturi pumps discharging air to the bottom of the tank for maintaining dissolved oxygen levels.

Flow from the oxidation ditch gravitates to a 15.2 m diameter radial-flow sedimentation tank fitted with a rotating half-bridge scraper mechanism. Settled sludge from this tank gravitates to a nearby sludge chamber. A sludge-lifting wheel in the sludge chamber returns part of the sludge as return activated sludge (RAS) back to the oxidation ditch to maintain the microorganism concentration.

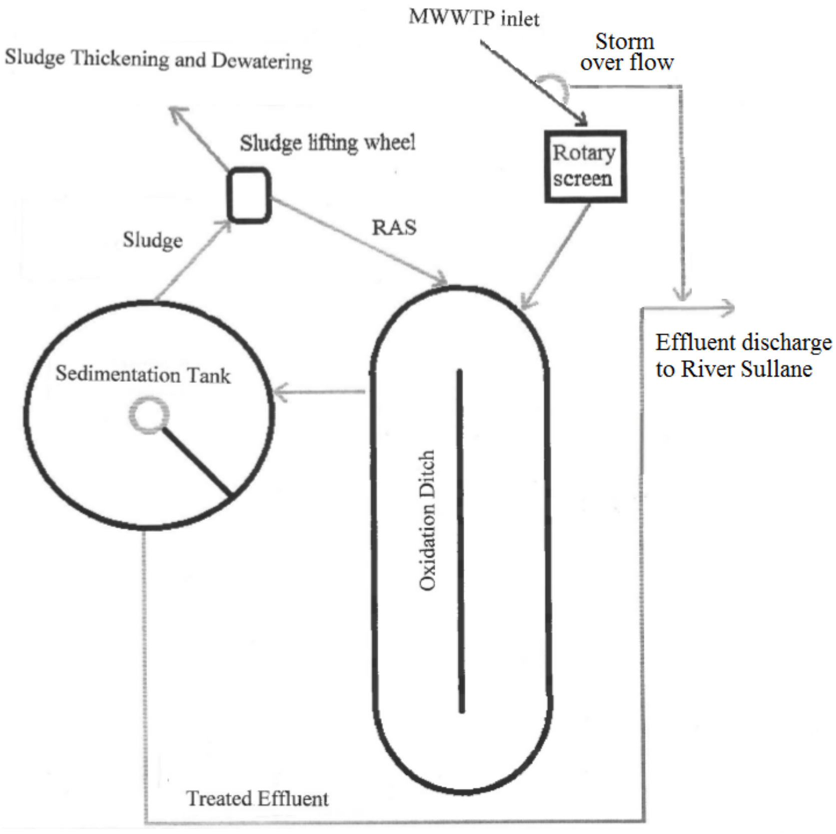


Figure 4.3.1: Macroom Wastewater Treatment Plant Schematic Diagram

Treated effluent, which overflows from the sedimentation tank, combines with the storm overflow, if any, and gravitates via an outfall pipe to the River Sullane. A submersible pump, installed in a sump adjacent to the sludge wheel chamber, pumps surplus sludge to a sludge holding tank followed by the sludge dewatering press.

The sludge thickener is a flat-bottomed fabricated steel tank in which a mixer is installed. The thickened sludge produced is pre-conditioned before dewatering using polyelectrolyte to improve its dewaterability. Supernatant liquors that overflow from the sludge thickener and filtrate from the dewatering press gravitate to the oxidation ditch. They combine with the incoming wastewater and receive complete biological treatment with the main process stream.

Struvia™ pilot plant demonstrator

The Struvia™ pilot plant has been designed and built by the technical department of Veolia Water, France, to facilitate the recovery of phosphorus contained in wastewater through a crystallisation/precipitation process.

The Struvia™ process highlighted in Figure 4.3.2 uses a crystallisation reactor where a patented mixer, TurboMix™, achieves rapid mixing in combination with lamella settlers to produce and separate crystals from the wastewater within a single tank with a small footprint, making it an economic phosphorous recovery process. TurboMix™ encourages crystallisation, and an integrated lamella settler ensures the separation of the produced crystals and the treated effluent.

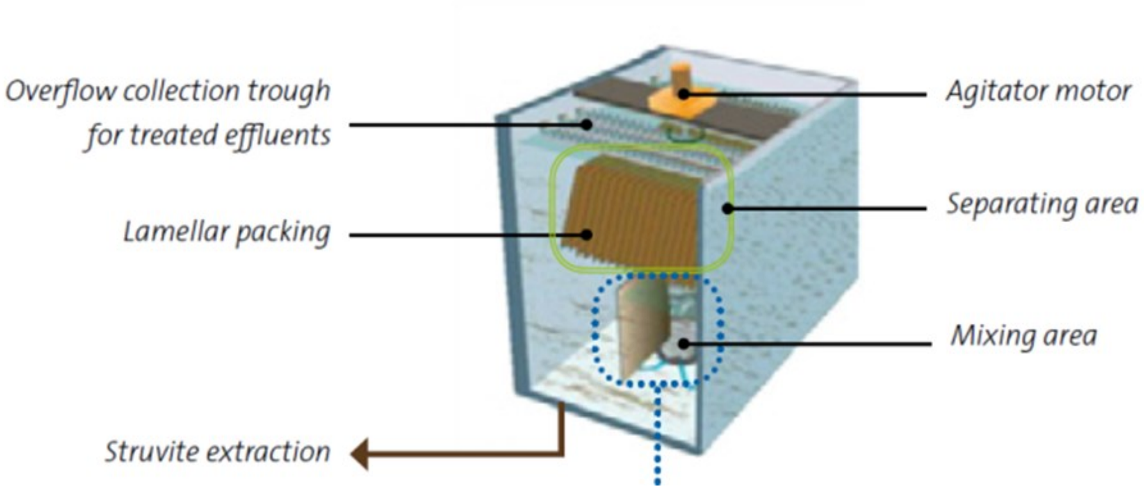


Figure 4.3.2: Struvia™ process crystallisation reactor with TurboMix™, and lamella settlers (Veolia Water Technologies 2016)

Jar tests

As part of the optimisation process, jar tests were conducted in the MTU laboratory on effluent waste samples obtained from the WWTP to investigate phosphorus removal, optimum pH, lime dose, stirring speed and settling time.

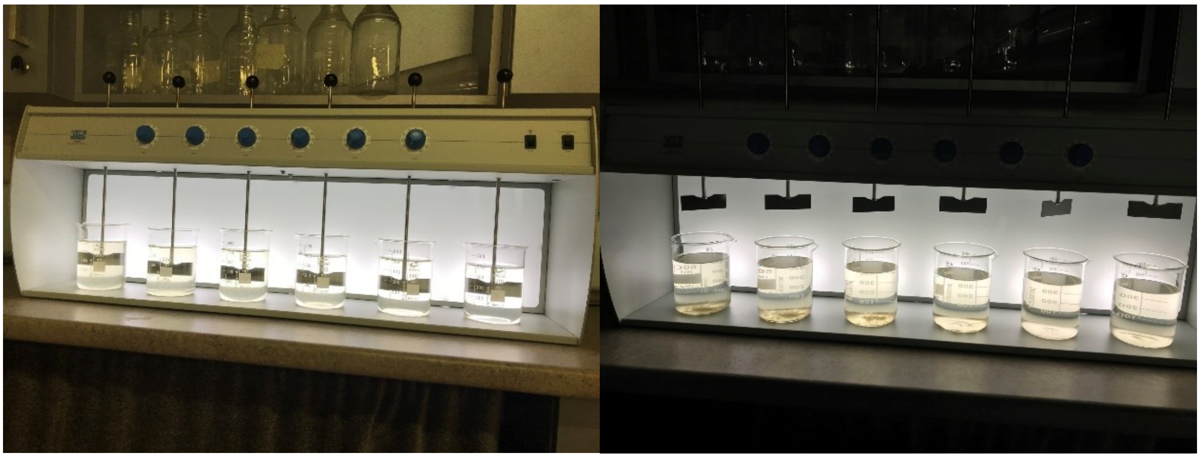


Figure 4.3.3: Jar test apparatus (Pictures: MTU)

Jar tests were conducted in batch experiments using lime addition on both a synthetic wastewater solution and the actual wastewater effluent from the WWTP.

Synthetic wastewater: A synthetic solution containing 20 mg/L phosphorus was prepared by dissolving reagent grade KH_2PO_4 in deionised water. This wastewater was poured into six glass jars to a volume of 500 ml. Increasing quantities of hydrated lime (commercial lime powder containing 95 % $Ca(OH)_2$) were added to each jar. Immediately after lime addition, synthetic wastewater solution was mixed with a stirrer at 200 rpm for 1 minute, followed by slow mixing at 60 rpm for 20 minutes to encourage flocculation of the precipitates in a jar test assembly shown in Figure 4.3.3. After mixing, precipitates were allowed to settle for 30 minutes, and then the supernatant in each jar was analysed for phosphorus concentration. The results of the jar test experiment using synthetic wastewater are presented in Table 4.3.1. The concentration of phosphorus was determined with the Hach DR 2800 spectrophotometer.

Table 4.3.1: Results of the jar test experiment using synthetic waste.

Beaker (500 mL)	Lime Dose (mg/L)	pH	PO_4-P concentration (mg/L)
1	100	9.68	3.1
2	200	10.03	2.4
3	300	10.28	1.5
4	400	10.47	1.1
5	500	10.78	0.9
6	600	10.93	0.5

Actual wastewater: Jar tests were also conducted on the treated effluent wastewater samples from the WWTP using the procedure outlined above and the results presented in Table 4.3.2. The results showed that the maximum P removal occurred at an optimum pH value of 10.8, at 400 mg/L of lime dose, giving a residual P concentration of 0.9 mg/L reduced from an initial P concentration of 3.6. With a pH value of less than 10, the removal efficiency decreased significantly. Figure 4.3.4 presents the precipitation of phosphorus in the jar test glass beaker.

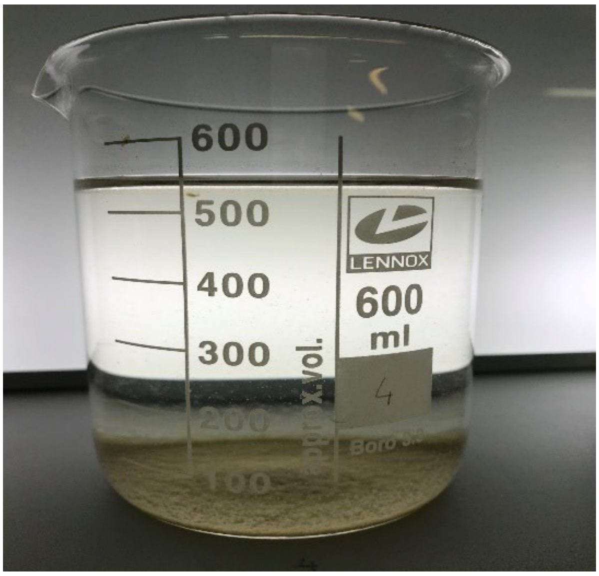


Figure 4.3.4: Phosphorus precipitation in a jar test glass beaker (Picture: MTU)

Jar tests established the initial pilot plant base settings as follows:

1. pH to be maintained at approximately 10.8
2. Hydraulic retention time to be maintained at 30 minutes

Table 4.3.2: Results of the jar test experiment using treated effluent from the WWTP

<table>
<tr><td colspan="4">Sample 1: Initial PO_4-P concentration = 3.6 mg/L</td></tr>
<tr><td>Beaker (500 mL)</td><td>Lime Dose (mg/L)</td><td>pH</td><td>PO_4-P concentration (mg/L)</td></tr>
<tr><td>1</td><td>80</td><td>8.61</td><td>3.1</td></tr>
<tr><td>2</td><td>160</td><td>9.73</td><td>2.9</td></tr>
<tr><td>3</td><td>240</td><td>10.19</td><td>2.5</td></tr>
<tr><td>4</td><td>320</td><td>10.56</td><td>1.3</td></tr>
<tr><td>5</td><td>400</td><td>10.80</td><td>0.9</td></tr>
<tr><td>6</td><td>480</td><td>10.95</td><td>0.9</td></tr>
<tr><td colspan="4">Sample 2: Initial PO_4-P concentration = 4.3 mg/L</td></tr>
<tr><td>Beaker (500 mL)</td><td>Lime Dose (mg/L)</td><td>pH</td><td>PO_4-P concentration (mg/L)</td></tr>
<tr><td>1</td><td>80</td><td>9.21</td><td>3.2</td></tr>
<tr><td>2</td><td>160</td><td>10.17</td><td>2.8</td></tr>
<tr><td>3</td><td>240</td><td>10.38</td><td>2.1</td></tr>
<tr><td>4</td><td>320</td><td>10.57</td><td>1.7</td></tr>
<tr><td>5</td><td>400</td><td>10.82</td><td>1.1</td></tr>
<tr><td>6</td><td>480</td><td>11.04</td><td>1.0</td></tr>
<tr><td colspan="4">Sample 3: Initial PO_4-P concentration = 3.1 mg/L</td></tr>
<tr><td>Beaker (500 mL)</td><td>Lime Dose (mg/L)</td><td>pH</td><td>PO_4-P concentration (mg/L)</td></tr>
<tr><td>1</td><td>80</td><td>8.93</td><td>2.6</td></tr>
<tr><td>2</td><td>160</td><td>9.77</td><td>2.1</td></tr>
<tr><td>3</td><td>240</td><td>10.14</td><td>1.5</td></tr>
<tr><td>4</td><td>320</td><td>10.38</td><td>1.2</td></tr>
<tr><td>5</td><td>400</td><td>10.85</td><td>0.9</td></tr>
<tr><td>6</td><td>480</td><td>11.10</td><td>0.8</td></tr>
</table>

4.3.2 Execution of I6.2

Installation

A site visit was made to Marquette-lez-Lille, France, on 6th December 2018 by MTU staff member to view the operation of the Struvia™ pilot plant and to review the overall requirements involved in establishing the pilot plant at the Macroom WWTP. Information was obtained on space requirements, electricity, water supply, waste discharge, legal aspects, insurance and health & safety requirements. This pilot plant was to be supplied on loan to MTU to investigate phosphorus removal and recovery from treated wastewater using chemical precipitation with lime at an Irish wastewater treatment plant. All the pilot plant equipment was installed in a lighted and heated container with a footprint of about 15 m^2, as detailed in Table 4.3.3.

Table 4.3.3: Container specifications with the Struvia™ unit

Parameter	Value
Length	6058 mm
Width	2438 mm
Height	2896 mm
Net empty weight	5 tonnes
Weight in operation	7.5 tonnes

A suitable location was identified for the pilot plant at the Macroom WWTP. Four precast concrete blocks of 600 mm x 600 mm were placed under each of the four corners of the container to create a solid foundation and to raise the plant, increasing protection against river flooding. The pilot plant container can be seen in Figure 4.3.5 and Figure 4.3.6.

A substantial part of the overall installation work was to fulfil the health and safety requirements set out by health and safety legislation. All works carried out were fully planned and risk assessed. A full risk assessment and method statement was drawn up comprising of both the installation and the operation of the pilot plant. All the requirements of Irish Water related to health and safety have been met. The health and safety document for the Struvia™ pilot plant was available onsite combined with the trial agreement for review by any visitor. It was, during the activity, a live document updated continuously to reflect any changes to process during the pilot plant operation, including an additional appendix to the document which assessed and reviewed issues which arose during the Covid-19 pandemic and lock down periods.

Figure 4.3.5: Struvia™ pilot plant container (Picture: MTU)

Figure 4.3.6: Internal view of the Struvia™ pilot plant container (Picture: MTU)

Pilot plant requirements

The pilot plant requires water, electricity, wastewater inflow and wastewater outflow services to be connected to the plant through the service hatch on the side of the container, as shown in Figure 4.3.7.

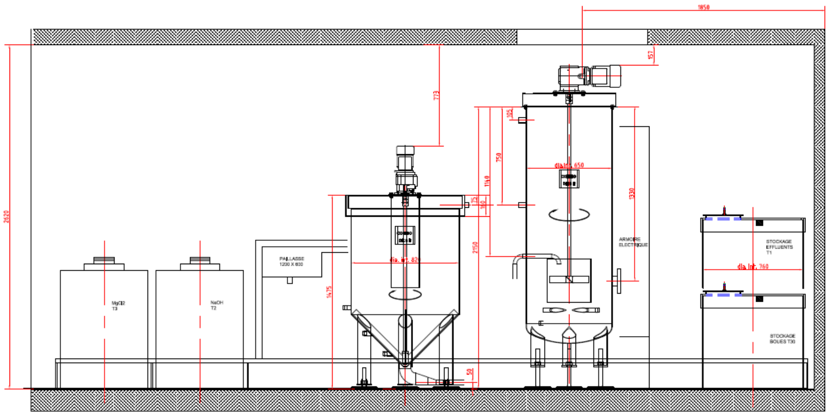
Figure 4.3.7: Struvia™ pilot plant service hatch (Picture: MTU)

Water supply: The water to the pilot plant is supplied from a tee off the water supply for the onsite welfare unit.

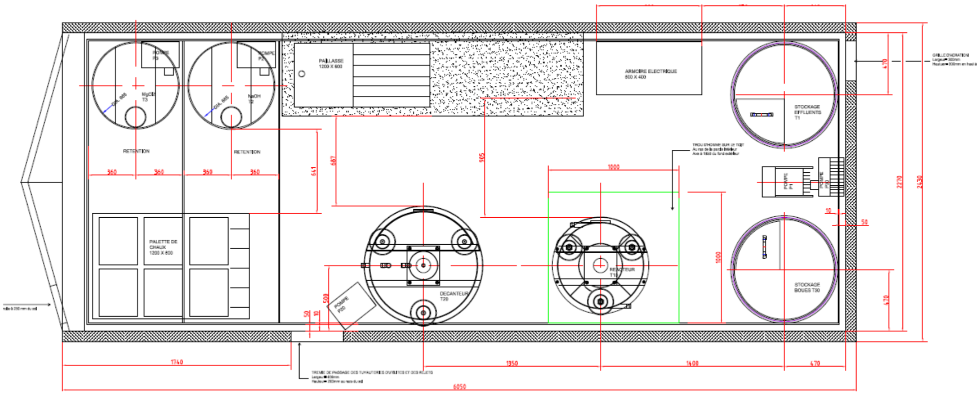
Electricity supply: The pilot plant requires a three-phase 5 kW power supply. This is supplied from an existing isolated socket attached to the side of the WWTP site office, thus ensuring that any fault occurring within the pilot plant will not affect the power supply to the WWTP.

Treated wastewater inflow: Treated effluent is lifted from the sampling well to the pilot plant using a 1200 W submersible pump secured within the flow of the WWTP outfall pipe. The effluent is pumped through a 35 m long section of 50 mm lay flat pipe that is connected to the influent inlet located in the service hatch on the pilot plant. The power supply to the submersible pump is controlled, and the PLC system regulates the flow in the pilot plant to maintain the wastewater level in the influent holding tank.

Treated effluent outflow: The treated effluent from the pilot plant is discharged back to the return activated sludge (RAS) sump. The treated effluent mixes with the RAS, where it flows directly back into the oxidation ditch for further treatment. The pilot plant layout is presented in Figure 4.3.8.



Pilot Plant side elevation



Plan veiw of pilot plant

Figure 4.3.8: Struvia™ pilot plant layout (Veolia, own illustration)

Pilot plant configuration

The treated effluent from the WWTP is pumped through a submersible pump to the pilot plant influent holding tank (T1), which is a polypropylene tank equipped with distribution and power cut solenoid valves. The wastewater is pumped from T1 into the stainless steel reactor tank (T10) using a peristaltic pump. The lime solution, stored in the tank (T2), is injected into the reactor tank T10 through a peristaltic pump controlled by the reactor pH via a control loop. When the reactor tank T10 is agitated, lime reacts with the phosphorus in the wastewater and precipitates calcium phosphate. The precipitate falls to the bottom of the reactor, while the clarified water rises to the top of the reactor passing through a laminar settler and overflowing into the decanter (T20). Automatic extraction of the wet precipitated calcium phosphate sludge is carried out from the reactor via a solenoid valve to a storage tank (T30) based on the total suspended solids (TSS) concentration in the reactor. Figure 4.3.9 shows a schematic view of the pilot plant.

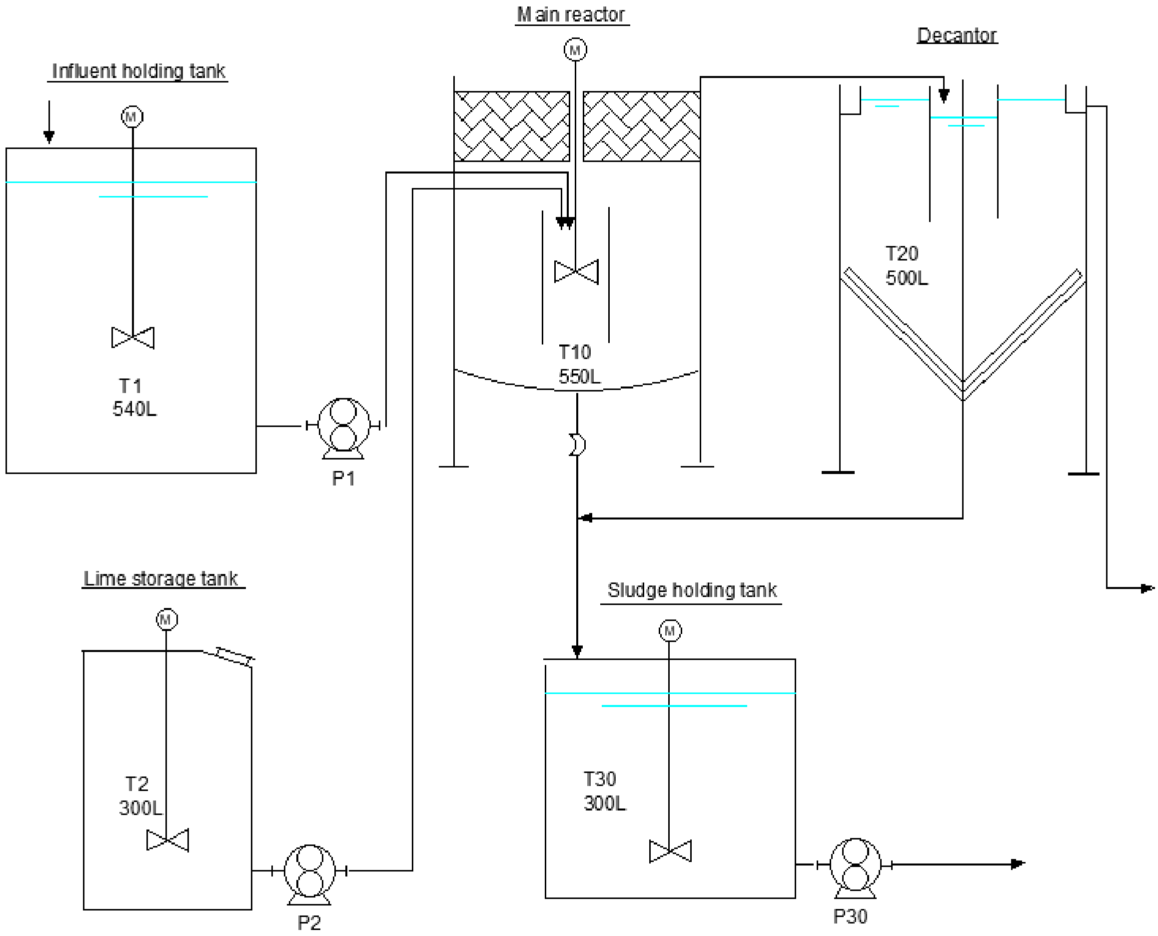


Figure 4.3.9: Simplified Struvia™ pilot plant schematic

Emergency procedures

The pilot plant is fully automatic, and the control panels can be seen in Figure 4.3.10. When it senses an issue, the plant will automatically shut off to prevent any damage. The plant is also equipped with an emergency stop switch located on the electrical cabinet indicated by an emergency stop tag. The emergency stop electrically shuts off the elements of the pilot plant such as feed pumps, reagent pumps, mixers etc.

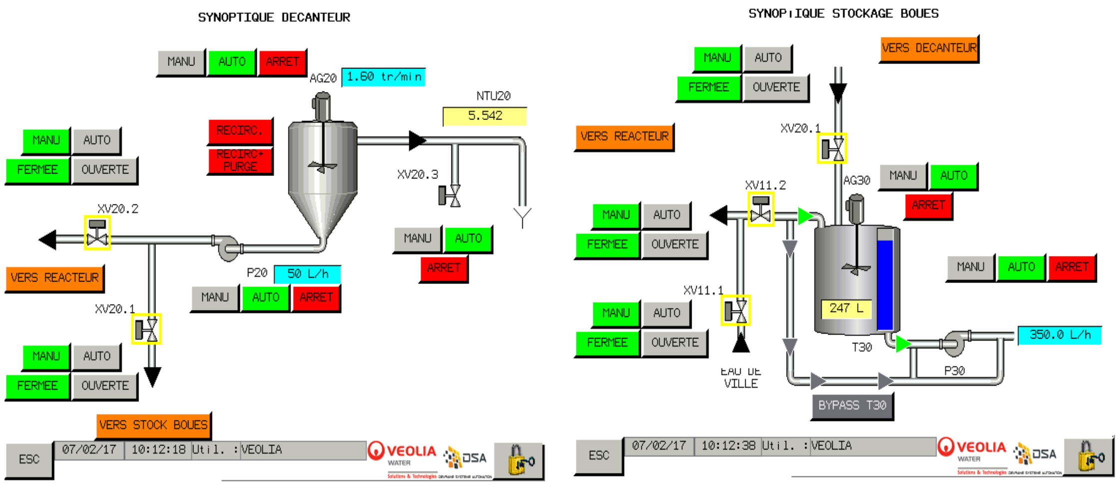


Figure 4.3.10: Computerised control station with automatic shut off system

Process description

The process recovers phosphorus from municipal wastewater through controlled precipitation of calcium phosphate (CaP) using lime. The chemistry of the process is comparable to conventional precipitation. By dosing a calcium salt (e.g. lime) to the wastewater, the solubility of CaP is exceeded, and subsequently, phosphate is transformed from the aqueous solution into solid material as fine dispersed, microscopic sludge particles. The different forms of CaP are Hydroxyl apatite (HAP) $Ca_5(PO_4)_3OH$; Amorphous calcium phosphate (ACP) $Ca_3(PO_4)_2$; Dicalcium phosphate (monetite) $CaHPO_4$ and Octacalcium phosphate (OCP) $Ca_4H(PO_4)_3$ $2.5H_2O$. The kinetics of CaP precipitation play a major role, as spontaneous precipitation of CaP from the wastewater does not occur. However, crystallisation of CaP can be achieved by adding seed crystals. The process flowsheet of the pilot plant is shown in Figure 4.3.11.

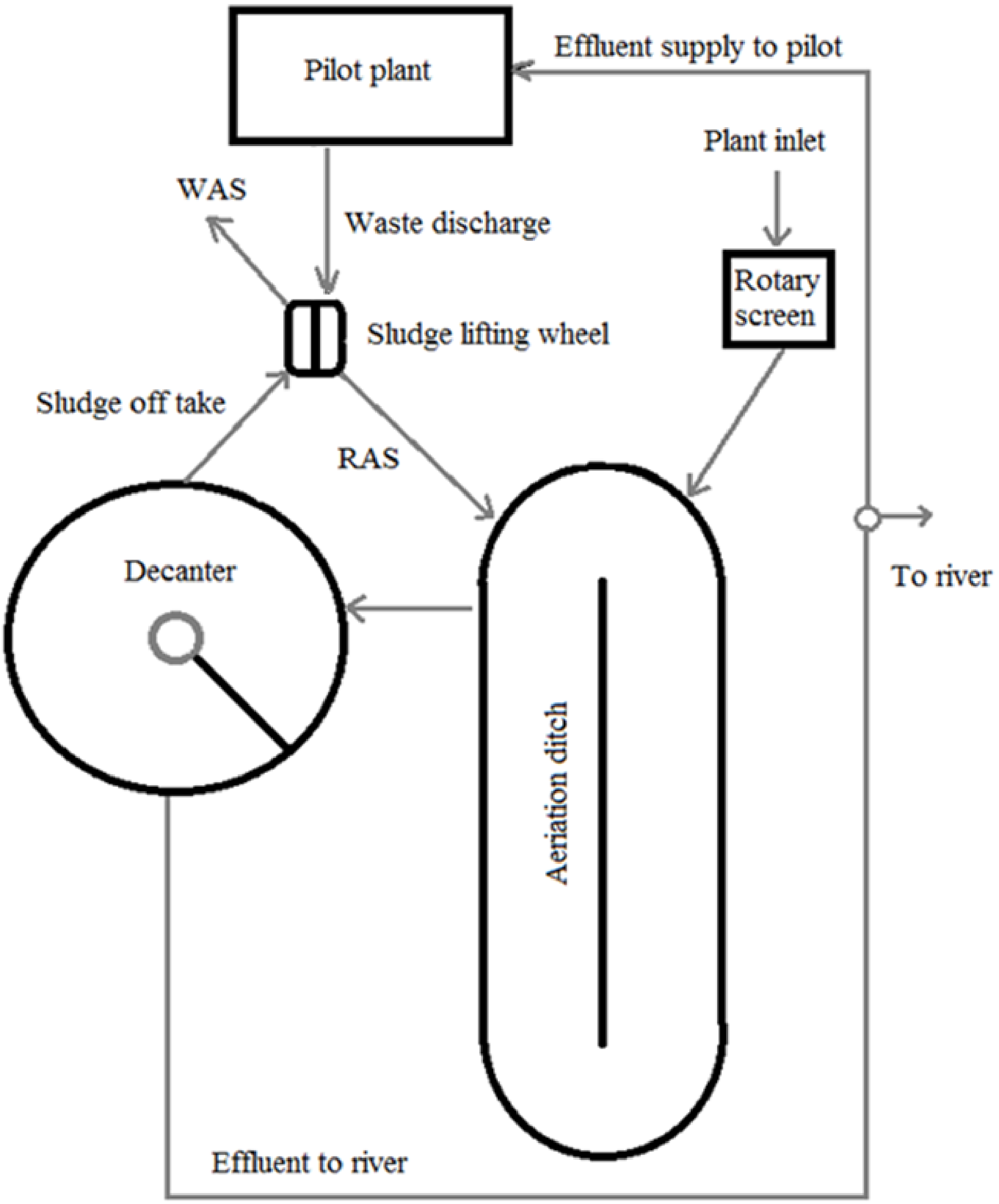


Figure 4.3.11: Process flowsheet for the Struvia™ pilot plant at the WWTP

Influent holding tank (T1)

Struvia™ reactor (T10)

Decanter (T20)

Sludge holding tank (T30)

Lime dosing system (T2)

Control cabinet

Figure 4.3.12: Components inside the Struvia™ pilot plant (Pictures: MTU)

In the Struvia™ reactor, the two-step precipitation and solid/liquid separation occur in the same device. The mixing zone is equipped with a vertical mixer/stirrer, a draft tube and several baffles to optimise the mixing and the chemical injection. Above the mixing zone is an integrated lamella settler to ensure the separation of the treated effluent and the precipitates. On-line probes for pH, turbidity and TSS are used to control the process. Figure 4.3.12 shows photographs of the different components of the pilot plant.

Pilot plant operation

The effluent from WWTP is pumped from the sampling well to the pilot plant, and the flow is regulated by the PLC system in the pilot plant. The waste is then pumped at 500 L/h in an upward direction through the cylindrical reactor into the mixing and reaction zone where 3 % lime solution is also injected and pH is controlled in the range 10.7 to 10.9 using a pH probe. The CaP precipitates are formed and grow in the reactor maintained at an HRT value of 30 minutes with a mixing speed of 100 rpm. Growing precipitates in the reactor are held in suspension and at the start, 3 kg of crushed limestone fines (100 – 200 µm size) was injected as seed material in the bottom of the reactor to initiate the establishment of a fluidised bed.

The fluidised bed enables CaP precipitates to grow and allows the bigger particles to settle in the conic bottom of the reactor. In contrast, the smaller particles are kept in the loop until they become large enough to settle. These precipitates subsequently settle and form sludge, which is discharged in a small quantity from the bottom of the reactor at regular intervals. A TSS probe records the average concentration of precipitates in the reactor. When a target concentration of TSS in the reactor is reached, the precipitates are drained and collected. In consultation with Veolia the solids extraction point was then set at 60 g/L and the suspended solids above this concentration are drained and collected out of the reactor.

These precipitates are dried to obtain a recovered P product, as shown in Figure 4.3.13. Lamella packing retains most precipitates in the mixing zone and the treated effluent from the top of the reactor flows into the decanter equipped with a scraper. Some precipitates settle at the bottom of the decanter and are pumped back to the reactor to promote precipitate growth. The supernatant of the decanter is checked for turbidity with a turbidity probe and discharged to the RAS sump to return to the oxidation ditch for further treatment.

Figure 4.3.13: Recovered P product from the pilot plant at the WWTP (Picture: MTU)

The pilot plant operation may be broadly defined in 6 stages as follows:

Stage 1 (4th November 2019 to 2nd December 2019)

The Veolia team visited Macroom Wastewater Treatment Plant (WWTP) in the last week of October 2019 to assist MTU staff with the start-up of the Struvia™ P-recovery demonstration plant. Work then commenced on the Struvia™ pilot plant on 4th November 2019 and 3 kilograms of crushed limestone fines (100 – 200 µm size) were added to the crystallisation reactor as a calcium-based seed material to establish the fluidised bed. It was challenging to commission and operate the pilot plant with approximately 30 to 35 site visits undertaken by two MTU team members on each occasion. The progress was slow due to complications in optimising fluidised bed development, stirring rate, lime dosing and flow rate control. A potential issue with the Struvia™ pilot plant was the lack of sludge output as precipitates/solids being colloidal do not settle and escaped out of the system. The lower sludge output may also be attributed to low concentrations of phosphorus in the effluent of the WWTP and low alkalinity in the pilot plant's influent, leading to a smaller amount of $CaCO_3$, causing a decrease in settleability of the flocs. Over 2 kilograms of the recovered P product was obtained and sent to the University of Ghent for quality assessment analysis on the 13th January 2020.

The fluidised bed could not be stabilised and a high amount of solids escaped with the effluent from the system leading to the temporary shutdown of the pilot plant on the 2nd December 2019. Total suspended solids (TSS) in the incoming treated effluent from the WWTP were in the range 10-20 mg/L, whereas the TSS going out with the effluent from the pilot plant was in the range 30-60 mg/L.

Stage 2 (27th January 2020 to 19th February 2020)

The Veolia Water team from France visited again in the 3rd week of January 2020 to assist MTU with the plant's restart and optimisation of the process. A new system for poly dosing was set up to inject cationic polymer at a dose of 0.4 mg/L in the influent to the main reactor to facilitate the floc formation and settling of fine precipitates. Several issues were encountered before achieving the entire operation of the process, including blockages to the lime dosing pipe, and improper functioning of valves, sensors and the submersible pump.

Work recommenced on the Struvia™ P-recovery demonstration plant on 27th January 2020 to ensure the optimisation and continued operation of the demonstrator unit. The bed was gradually established and stabilised until 19th February 2020. The restart process, commissioning and optimisation process was very challenging, but the pilot plant became fully operational to establish the fluidised bed with promising outcomes. The Struvia™ pilot plant was initially ran during the daytime before being subsequently operated continuously for periods up to one week.

Stage 3 (20th February 2020 to 27th November 2020 – including pre and post-Covid lockdown periods)

The Struvia™ P-recovery demonstration plant operated continuously and was working satisfactorily at a steady-state before it was closed down on 12th March 2020 due to Covid-19 restrictions under a directive from Irish Water, the owner of WWTP. 40 to 45 site visits to the WWTP took place over the period from 27th January 2020 to 12th March 2020. The waste stream contains low concentrations of P, making direct recovery of phosphorus technically challenging. The lower sludge output may also be attributed to the low alkalinity in the pilot plant's influent, leading to a smaller amount of $CaCO_3$, causing a decrease in settleability of the flocs. The waste samples were collected and analysed in the MTU laboratory for pH, alkalinity, total suspended solids, COD, phosphorus and total nitrogen content. The TSS concentration in the effluent from the pilot plant was maintained in the range of 15-25 mg/L. The average pH of the pilot plant effluent was 10.37. The recovered P product was harvested daily, and approximately 15 kilograms was obtained, of which approximately 5-6 kilogram has been used at MTU in field and pot trials for quality assessment. Following a lengthy health and safety assessment process, permission was granted to restart operations at Macroom WWTP. Testing recommenced on 18th November 2020. The plant was recommissioned over two days before being operated at pH 10.80 for an additional six days.

Stage 4 (26th November 2020 to 22nd December 2020)

This involved operating the pilot plant at incrementally lowered pH levels, in a bid to reduce pilot plant inputs. The work focused on reducing the quantity of hydrated lime being used within the system, as hydrated lime has a high carbon footprint. Previous jar test experiments have highlighted that varying levels of P removal occur at or above a pH of 10.0. To review the effects of P removal and recovery at varying pH levels, a research plan was devised to incrementally lower the pH levels of the plant to 10.6, 10.4 and 10.0. At each incremental pH level, it was intended to operate the plant for at least one week.

Stage 5 (11th January 2021 to 20th January 2021 – Testing of recycled products)

Stage 5 consisted of replacing hydrated lime with recycled calcium products to reduce the overall carbon footprint of the recovery process. Preliminary jar tests indicated that recycled plasterboard (gypsum) could remove sufficient quantities of P when combined with equal amounts of hydrated lime. Testing commenced on the inclusion of recycled calcium products in the pilot plant from 11th January 2021 and concluded on 20th January 2021.

Stage 6 (11th February 2021)

Comprised of the pilot plant shutdown and decommissioning process. It was conducted over four days commencing on 11th February 2021.

4.3.3 Analyses of results of I6.2 operation

The phosphorus concentration in the WWTP is reduced by conventional sewage treatment from 10 - 12 mg/L in the raw sewage to 3-4 mg/L in the treated effluent. The pH values and phosphorus concentrations of the influent and effluent wastewater samples of the pilot plant were analysed in stage 1 operation and the results are shown in Table 4.3.4.

Table 4.3.4: Influent and effluent samples analysis for the pilot plant in stage 1

Day	Influent waste to the pilot plant		Effluent waste from the pilot plant	
	pH	PO_4 concentration (mg/L)	pH	PO_4 concentration (mg/L)
12-Nov'19	6.80	3.6	10.85	1.5
13-Nov'19	6.91	3.4	10.90	2.0
15-Nov'19	6.90	4.0	10.82	1.9
20-Nov'19	6.85	3.9	10.93	1.6
21-Nov'19	6.83	3.2	8.11	2.9
26-Nov'19	6.90	3.8	10.93	1.5
27-Nov'19	7.01	3.1	10.84	1.1
28-Nov'19	6.98	3.8	10.98	1.4
29-Nov'19	6.93	2.9	9.35	2.1

In stage 2 of operation of the pilot plant, the fluidised bed was gradually stabilised until the 19th February 2020, except for some problems encountered on 12th February 2020 due to flooding caused by extended periods of heavy rain fall resulting in flooding in the river channel. The rising river level backed up the effluent outfall pipe causing the pilot plant influent to became diluted with river water. Flood levels receded over a period of 24 hours normalising pilot plant operations after which the pilot plant worked satisfactorily until the shutdown of the pilot plant on 12th March 2020 due to Covid-19. The results of the fluidised bed establishment are shown in Figure 4.3.14.

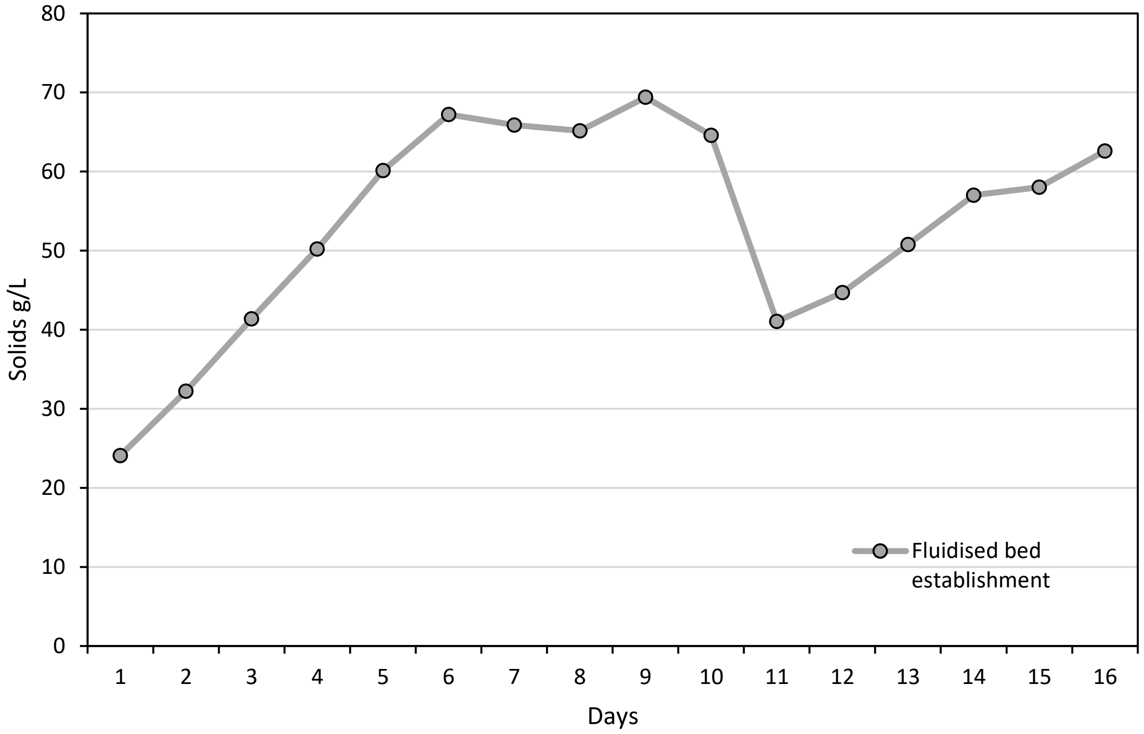


Figure 4.3.14: Establishment of the fluidized bed in the reactor

During stage 3, the pilot plant operated at pH 10.8 for 11 days before the Covid 19 shut down and for an additional 6 days following the recommencement of testing on the 18th of November 2020 during which 17 pilot plant influent and effluent samples were taken and analysed. Throughout the testing process, the pilot plant had an average influent phosphate content of 4.26±1.29 mg/L. Through the precipitation of calcium phosphate, the effluent PO_4^{3-} content was reduced to 1.70±0.54 mg/L resulting in a P removal of 60.26 % with the lowest P concentration of 0.9 mg/L being achieved, the influent and effluent PO_4^{3-} concentration is presented in Figure 4.3.15. Overall a uniform and consistent pattern of PO_4^{3-} removal occurred when operating at pH 10.8 with effluent P concentration mirroring the influent P concentration but with an average reduction of 2.58 mg/L.

It may be noted that it is estimated that Irish WWTPs discharge up to 1475 tonnes of P to receiving waters annually, impacting on water quality and effectively wasting P (8). This would suggest that a national rollout of this P-recovery technology (for approximation purposes and cognisant of the broad assumptions made) would indicate a recovery rate of over 900 tonnes.

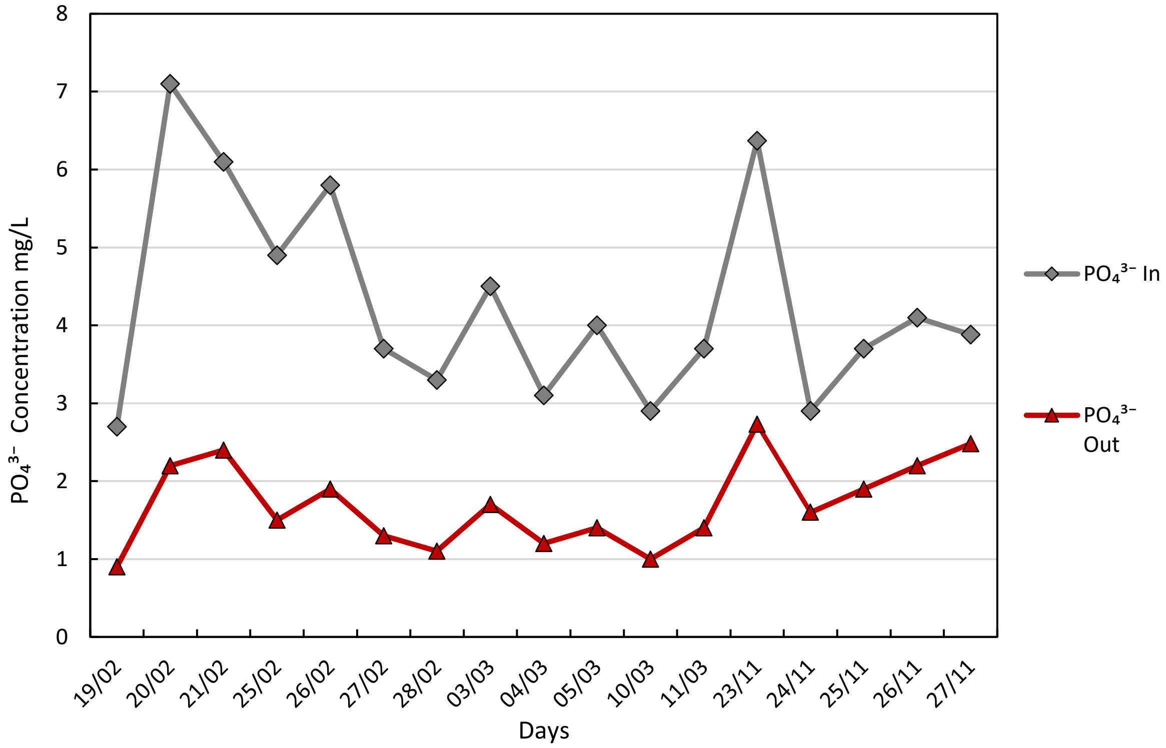


Figure 4.3.15: Change in phosphorus concentration during operation of the Struvia™ pilot plant starting the 19th of February 2020

Throughout the pilot plant operation, it was evident that a considerable quantity of nitrogen was removed from the pilot plant influent, as presented in Figure 4.3.16. The true nature of the nitrogen removal by the pilot plant is not fully understood. Some of the nitrogen may be released to the air as ammonia gas, a process which is encouraged by the agitation of the influent carried out within the influent holding tank (T1) and the main reactor (T10). The most probable route for the vast majority of nitrogen removal is through the co-precipitation and binding of the colloidal organic matter along with the COD.

On average, over 3.67 mg/L of total nitrogen was removed from the pilot plant influent through the methods highlighted above, this resulted in a total nitrogen removal efficiency of 17.6 %. Nitrogen removal was not the target of this exercise; however, it proved to be highly beneficial in the context of the overall discharge limits of the pilot plant.

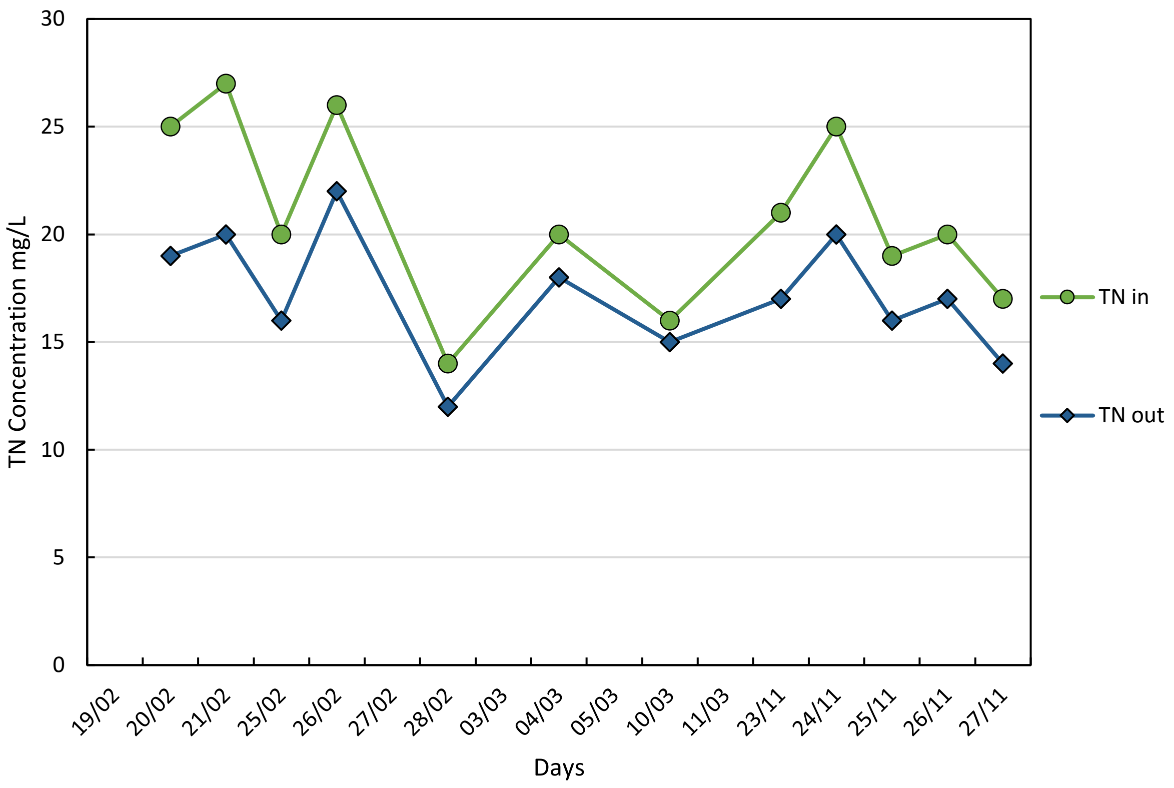


Figure 4.3.16: Change in total nitrogen concentration during operation of the Struvia™ pilot plant starting the 19th of February 2020

Chemical oxygen demand removal (COD) is calculated by testing the inlet and outlet samples from the pilot plant. The organic matter held COD is co-precipitated with calcium to create heavy solids trapped within the reactor or, to a greater extent, settled within the clarifier. In both cases, the COD is generally removed with the recovered material as organic matter. Over the running period of pH 10.8, there was an average COD removal of 34.12 mg/L, a reduction of 38.72 %. The overall COD reduction followed a similar trend to that presented for P removal. The effluent COD level mirrored the pilot plant influent COD concentration but at a lower level. The COD influent and effluent concentrations are shown in Figure 4.3.17.

The removal of COD through the recovered material as organic material reduced the overall COD and suspended solids loading of the outgoing effluent. This is beneficial in assisting the WWTP in meeting its discharge limits; however, the inclusion of high levels of organic material in the recovered product poses some issues for the recovered product itself. The organic material dilutes the recovered product reducing the P content of the material and possibly introducing high levels of pathogens and toxins to the recovered material. The degradation of volatile solids within the recovered material may result in the production of odours coupled with higher levels of material requiring dewatering and drying.

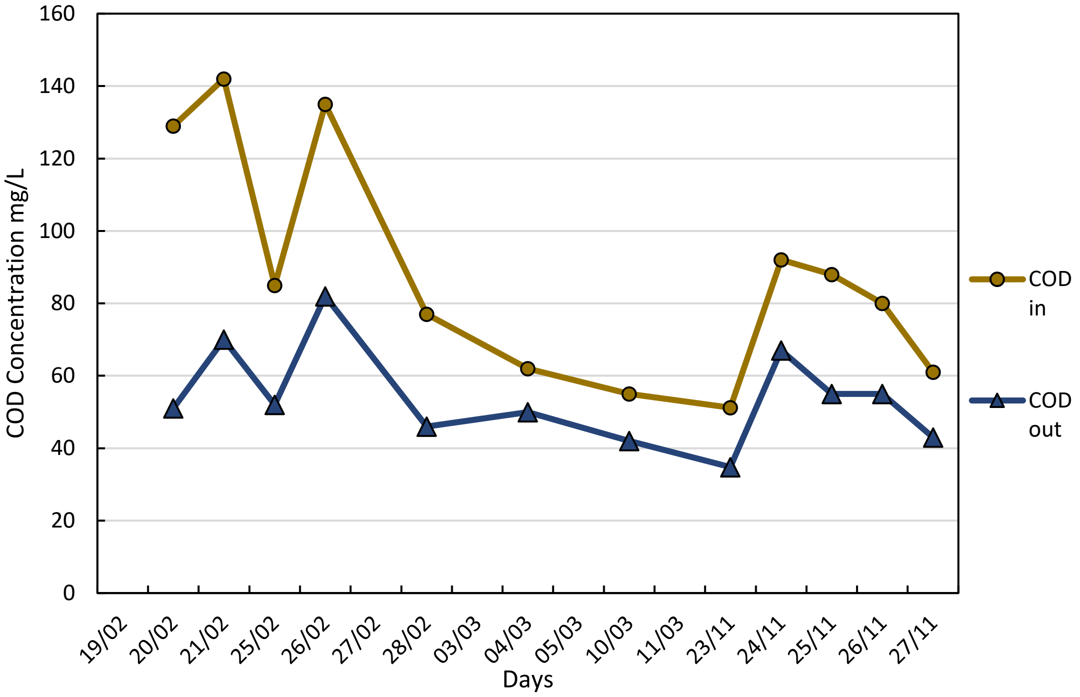


Figure 4.3.17: Change in COD during operation of the Struvia™ pilot plant starting the 19th of February 2020

The inclusion of lime increased the alkalinity of the effluent from 54 mg/L to 81.5 mg/L, as shown in Figure 4.3.18. This increase in alkalinity may be linked to the rise in pH due to the addition of lime. Further investigations are needed to adjust the pH of the treated effluent from the pilot plant to meet the discharge limits prior to its discharge to the environment.

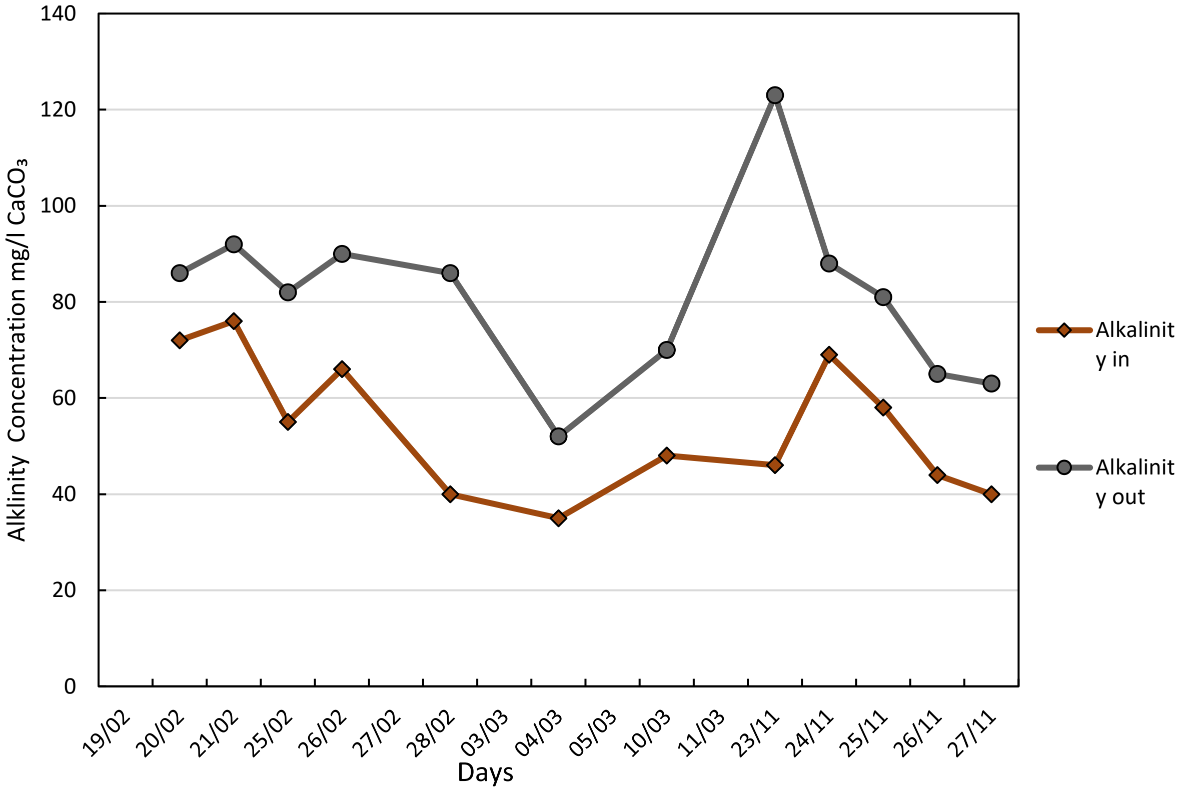


Figure 4.3.18: Change in alkalinity during operation of the Struvia™ pilot plant starting the 19th of February 2020

4.3.3.1 *pH reduction*

Preliminary jar tests highlighted that P precipitation and removal occurred at or above pH 10 with the most favourable PO_4^{3-} removal occurring at a pH of 10.8, with effluent PO_4^{3-} concentration reducing below 1 mg/L. The pilot plant pH was reduced to 10.6 before being sequentially dropped to pH 10.4 and pH 10. At each level, the plant was operated continuously for at least five days. PO_4^{3-} removal was observed during the operation at pH 10.6, with an average removal of 0.45 mg/L PO_4^{3-} occurring. The removal resulted in a 24.5 % reduction in influent P content, which is almost two and half times less than the P removal at pH 10.8.

The pilot plant was operated at a pH of 10.4 for six days as a mechanical failure occurred, necessitating the extension by one day. P removal patterns were reduced substantially during the operation period, with evidence of P removal only occurring on three out of the six days of operation as noted in Figure 4.3.19. On the other three days, the pilot plant effluent presented a higher P level than the pilot plant influent. This appears to have been caused by the fluidised bed eroding, releasing the previously captured phosphorus to the solution, increasing the effluent P content and degrading the bed. This bed erosion is evidenced by an increase in the TSS (for a pH range of 10.0 to 10.4) with an average influent TSS of 18.1mg/L and an average effluent TSS of 30.2 mg/L.

Over the five days of operation at pH 10.0, no reduction in P was observed. In contrast, the pilot plant effluent presented an effluent P content higher than the pilot plant influent. Again this may be attributed to extensive bed erosion.

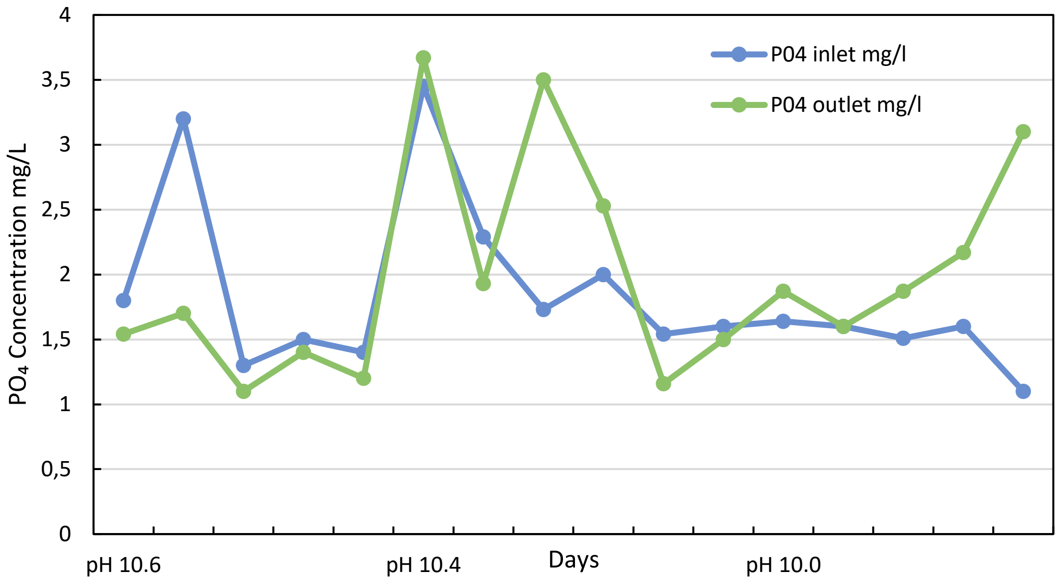


Figure 4.3.19: PO_4^{3-} removal at pH 10.6, 10.4 and 10.0 testing started 26th of November 2020

No substantial or consistent pattern of nitrogen removal occurred at either pH 10, 10.4 or 10.6 with only a marginal reduction over the entire duration of the highlighted trial period of 1.75 mg/L. This decrease is not significant in the context of the overall data set, indicating that the plant is unsuitable for nitrogen removal below pH 10.8. For COD removal, a slight reduction occurred during pH 10.6 of 1.26 mg/L resulting in a 8 % reduction of COD, which is not significant to previous COD removal at pH 10.8, which had a COD removal of 38.72 %. When the pH was adjusted to 10.4, a substantial increase in COD content in the pilot plant effluent was observed, after which the effluent's COD content declined and continued to decline into the testing phase for pH 10.0. From reviewing the data, it is suggested that the elevated COD level resulted from the bed erosion with a lower pH reducing the bonds between the COD and the calcium releasing the COD to the solution.

4.3.3.2 *Combined results*

Hydrated lime is the most considerable input into the recovery process and is automatically injected into the reactor as a 3 % solution to maintain the reactor pH. The lime storage tank was refilled daily with water, and the relevant quantity of hydrated lime was gradually added by weight, allowing time for the inbuilt mixer to blend sufficiently. Lime usage is dependent on the dilution rate of incoming WWTP effluent, pH and organic matter content. The daily lime usage was determined by recording the volume of lime solution used over 24 hours. Lime usage varied over the operation period from a maximum of 120 L per day to a minimum of 20 L per day, corresponding to a dry lime usage of 3.6 kg and 0.6 kg, respectivelyn average, 90.7 L of the lime solution was used per day, equating to a dry lime mass of 2.72 kg. The daily 3 % lime solution usage is presented in Figure 4.3.20.

The daily lime usage of 2.72 kg for an effluent volume of 12 m^3 may be converted to an estimated lime usage requirement for the full Macroom WWTP for the AER flow rate of approximately 1300 m^3/day. The total annual lime requirement is approximately 108 tonnes which at a lime cost of € 200 per tonne would yield a total annual lime cost of approximately € 21,500.

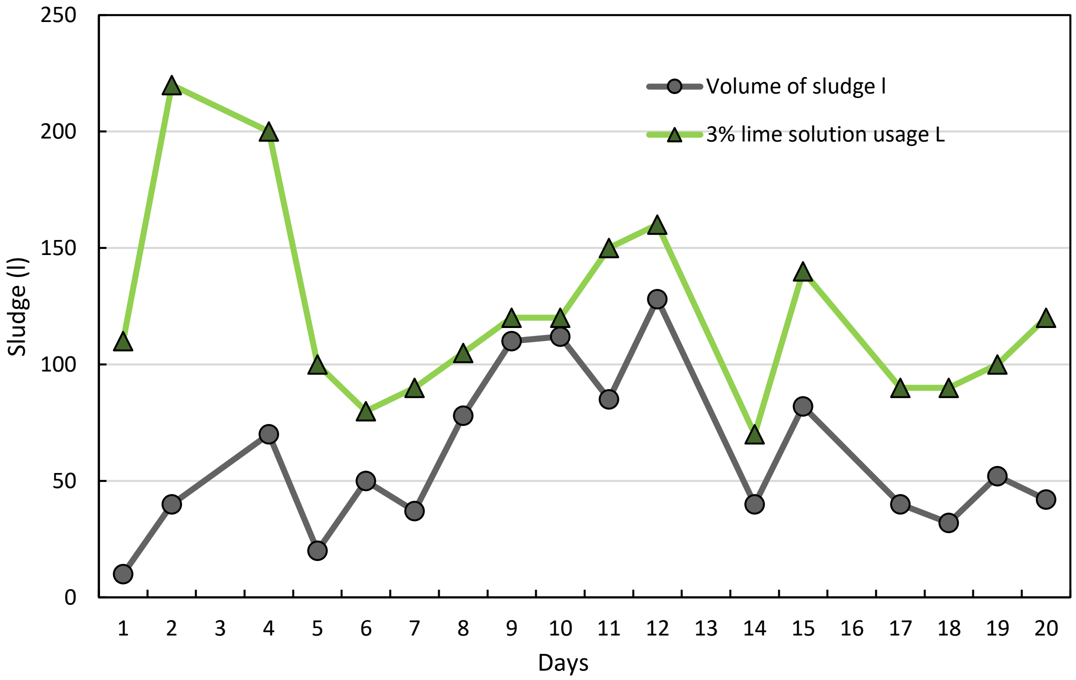


Figure 4.3.20: Lime usage verse sludge production starting the 19th of February 2020

Solids production is the fluid measure of the wet recovered material in litres, removed from the reactor daily. During the optimisation phase, solids were produced on 20 of the 35 days of operation. Solids removal occurred at a reactor solids concentration at or above 60 mg/L. Most solids were produced over the trial period, at pH 10.8. The reactor's solids concentration only reached the abstraction point of 60 mg/L, twice during pilot plant operations at pH 10.6 and did not occur at pH 10.4 or 10.0.

Over the trial period at pH 10.6 and 10.8, the average recovered material production was 56.2 L/day with a maximum material production of 128 L/day occurring. A clear relationship was observed between solids production and the 3 % lime solution dosage rate, with the solids production trend mirroring the lime dosage rate, as presented in Figure 4.3.20. The result is somewhat anticipated as the majority of the recovered product is formed of calcium.

To determine the pilot plant cumulative water usage a 13 mm inline Altecnic single jet water meter was installed on the 13th of November 2020.Over the 19 days of operation the pilot plant had a cumulative water usage of 2,345 L. This resulted in average daily water usage of 123.4 L of water. The primary source of water usage was for the lime dosage system, which used an average of 90.7 L of water daily with the remaining water was used for general cleaning maintenance (Figure 4.3.21).

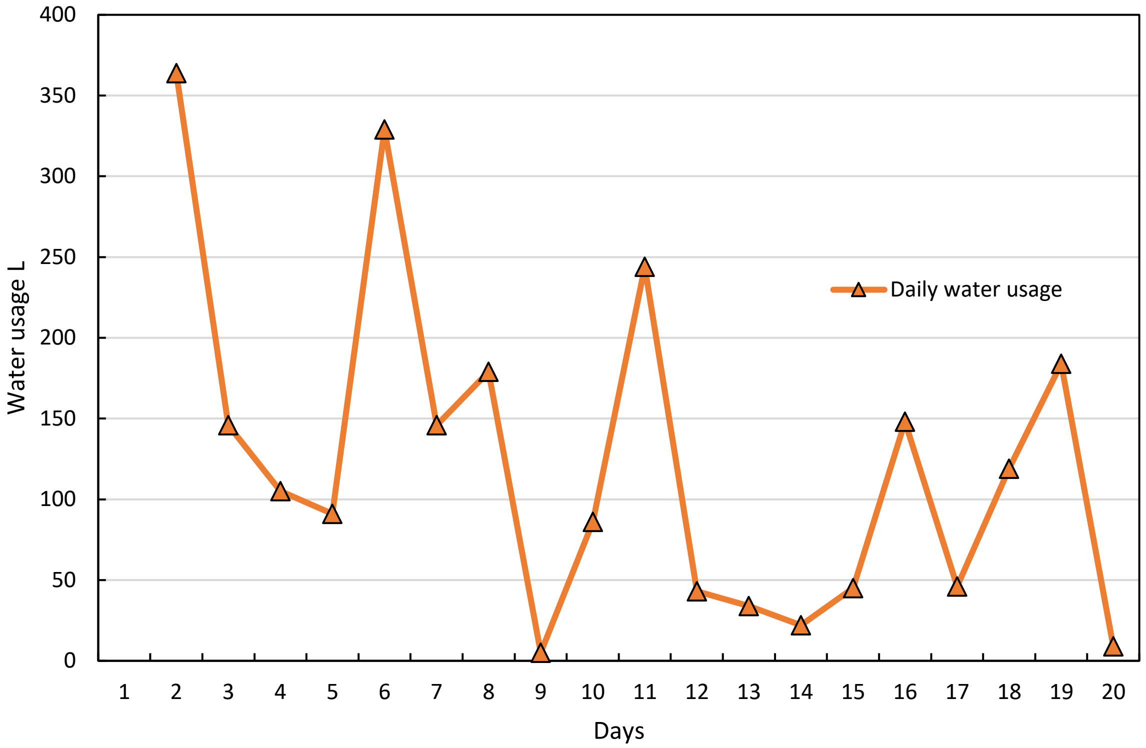


Figure 4.3.21: Water usage measurement started on the 24th of November 2020

A series of jar tests were conducted to test the feasibility of using locally sourced recycled calcium products to recover P using the Struvia™ pilot plant, to reduce lime use and increase the sustainability of the recovery system. All calcium products selected for testing were derived from waste materials produced at a sustainable scale within 100 km of the Munster Technological University, Bishopstown campus. The recycled calcium products were oyster shell, wood ash, bone char and gypsum plasterboard. The P removal ability of each recycled product was assessed in a series of jar test experiments, as shown in Figure 4.3.22. The jar tests indicated that locally sourced ground plasterboard gypsum provided sufficient quantities of calcium to induce precipitation and crystallisation of P once the additional pH correction was conducted. Altering the pH level onsite with the Struvia™ reactor is possible but it requires additional chemicals, adding additional costs and extra layers of complexity to the recovery system.

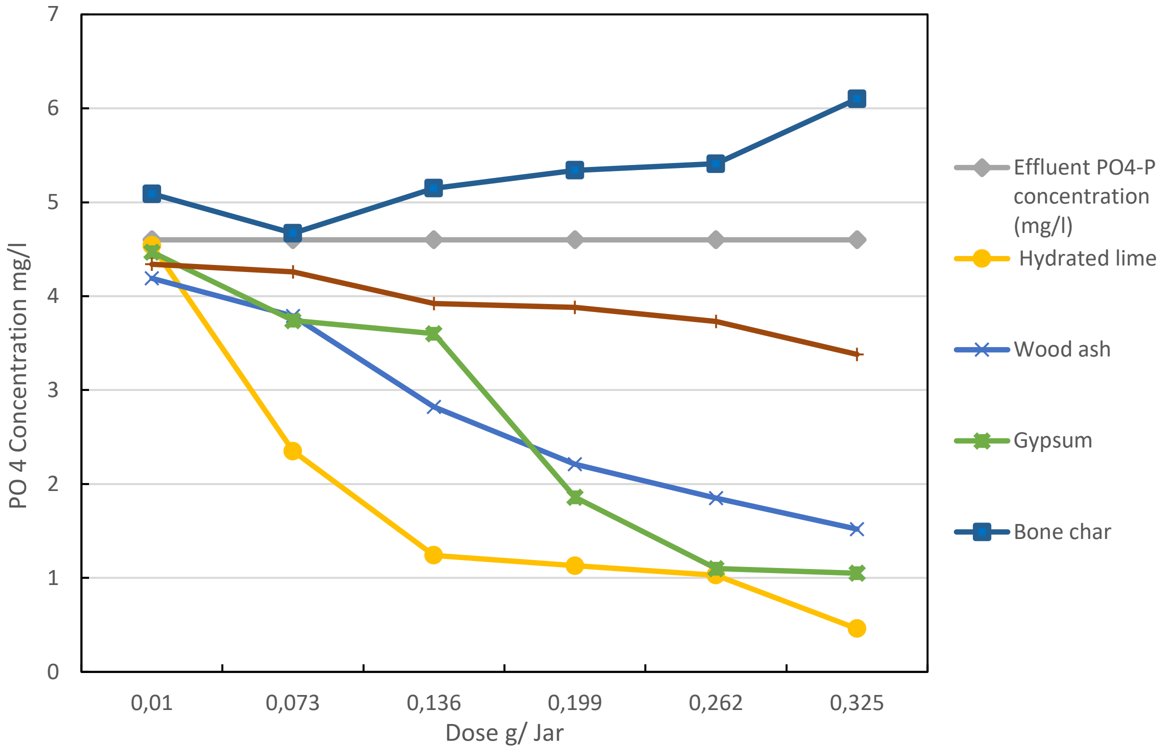


Figure 4.3.22: P removal using recycled calcium products with additional pH adjustment

Investigations revealed that an equal blend of recycled gypsum and hydrated lime could raise the pilot plant's influent pH level sufficiently to stimulate P removal. Initial jar tests indicated that a PO_4^{3-} of below 1 mg/L could be obtained using this method, as shown in Figure 4.3.23. Full-scale pilot plant tests were conducted to include recycled gypsum in the pilot plants lime injection system. Over two weeks, many unsuccessful attempts were made to modify the existing pilot plant mixing and injection system to dose the gypsum and lime solution successfully. The gypsum powder has a high specific gravity, leading to excessive sedimentation of the gypsum powder within the lime storage tank. Numerous processes were trialled to keep the gypsum powder in suspension, including increasing the mixing speed and inclusion of compressed air. None of the trialled techniques could successfully maintain the gypsum in suspension, allowing it to be injected into the pilot plant reactor. It may be concluded that, with the constraints of the automated pilot plant process, it is unsuitable for injecting gypsum or other dense materials into the pilot plant reactor.

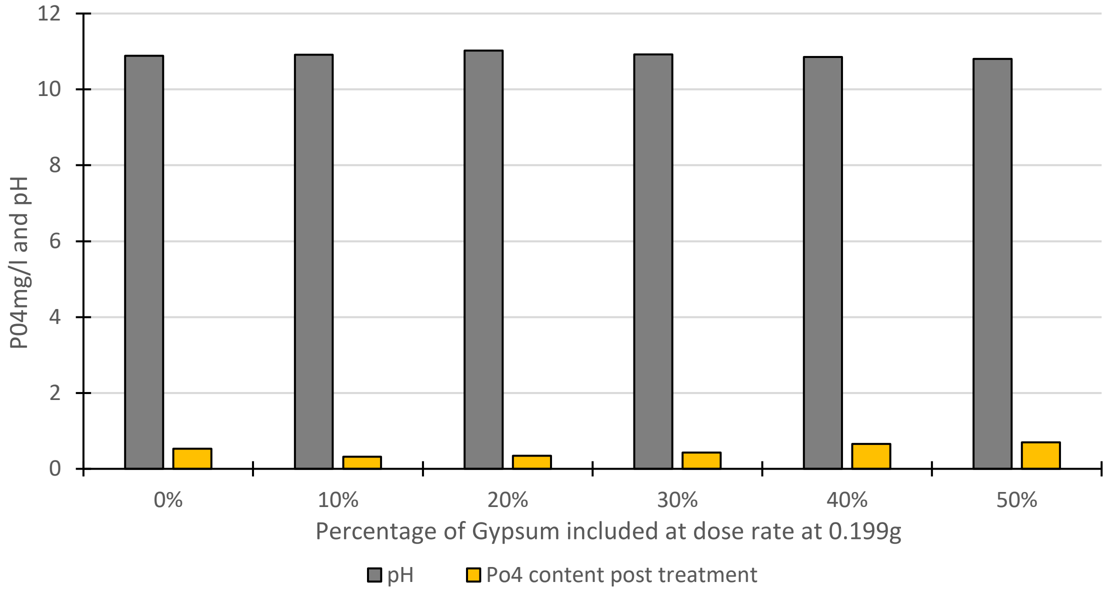


Figure 4.3.23: Incremental gypsum inclusion at 0.199 g/jar, with initial PO_4^{3-} concentration of 4.5 mg/L

4.3.4 Discussion of results for I6.2 operation

The commissioning process took longer than initially anticipated due to complications in establishing the fluidised bed and the loss of suspended solids with the effluent from the pilot plant. It took several weeks to refine the mechanical and physicochemical processes to match the pilot plant characteristics. The Struvia™ pilot plant operation in stage 1 had to be temporarily shut down on the December 2nd 2019 due to complications in optimising the process and in anticipation of the 2nd visit from the Veolia personnel required for assistance.

In Stage 2, the suspended solids content of the fluidised bed stabilised between 60 and 70 g/L for a sufficient period suggesting that the reactor had reached a solids equilibrium.

Once Stage 3 commenced, the plant worked efficiently within the project constraints. The steady-state operation was conducted over four weeks, with recovered product harvesting conducted daily. The removal and recovery of phosphorus led to the simultaneous reduction in total nitrogen and COD content of the wastewater. The effluent from the pilot plant has an elevated pH and alkalinity, the broader effect of which will require further investigation. The discharge of effluent wastewater from the pilot plant will have no impact on the operation of the WWTP as its flow rate is almost negligible compared to the total inflow received by the WWTP.

The recovered P product has an approximate 4.6±0.2 % P_2O_5 content. Further analyses are being conducted to determine the plant bioavailability and contaminant concentrations to evaluate its potential as a fertiliser.

Some P removal was observed during stage 4 operations. However, the research highlighted that the most suitable operating pH is 10.8. Recycled calcium products like gypsum plasterboard have the possibility to remove and recover P from municipal wastewater streams. The Struvia™ pilot plant is not configured correctly to allow for efficient and consistent injection of a Gypsum solution.

4.3.5 Conclusion for I6.2

The following are the primary conclusions based on the Demonstrator I6.2 which was undertaken to investigate the process of phosphorous removal and its recovery from municipal wastewater based on the Struvia™ Technology at the Macroom Wastewater Treatment Plant using lime for chemical precipitation.

1. Overall, this demonstration has provided significant insight into the effectiveness and limitations of the Struvia™ process through installation at the Macroom WWTP.
2. The primary benefits of the Struvia™ process are its simplicity and flexibility of application; lower demand for chemicals, production of recovered P from wastewater, reduction in P emissions and overall improvement to the environment.
3. The pilot plant operated most efficiently at a pH of 10.8 and less so in the range from 10 to 10.4.
4. The pilot plant has operated successfully at Macroom WWTP, reducing the wastewater PO_4^{3-} content from 4.28 mg/L to 1.70 mg/L, resulting in a removal efficiency of 60.26 %, as shown in Table 4.3.5.
5. The removal and recovery of phosphorus led to a simultaneous reduction in total nitrogen and COD content of the effluent. The effluent from the pilot plant has an elevated pH and alkalinity, the broader effect of which will require further investigation.
6. The Struvia™ operation at the Macroom WWTP produced approximately 60 kg of dry recovered calcium phosphate.

7.

Table 4.3.5: Summary of results at pH 10.8

Results	
PO_4^{3-} removal mg/L	2.58
PO_4^{3-} removal %	60.26 %
TN removal mg/L	3.67
TN removal %	17.60 %
Increase alkalinity mg/L	27.42
% increase in alkalinity	50.69 %
COD removal mg/L	34.12
COD removal %	38.72 %
TSS removal mg/L	7.50
TSS reduction	23.15 %
TSS (influent) mg/L	32.34
TSS (effluent) mg/L	24.49

8. A potential issue with the Struvia™ pilot plant is the lower sludge output, which may be attributed to the relatively low phosphorus content in the WWTP effluent.
9. The average pH of the effluent from the pilot plant was 10.37 (for a pilot plant pH of 10.8). This pH level exceeds the Macroom WWTP Emission Limit Value (pH from 6 to 9) and thus for a full-scale P-recovery plant pH correction would be required.
10. The scale up of the P-recovery process to the full WWTP would involve a total annual lime requirement of approximately 108 tonnes which at a lime cost of € 200 per tonne would yield a total annual lime cost of approximately € 21,500.
11. The results presented in this report for the Struvia™ pilot plant operation at the Macroom WWTP indicate satisfactory pilot plant effluent parameter values (relative to the Emission Limit Values for the Macroom WWTP) for COD, TSS and PO_4^{3-} but not for pH (Cork County Council 2008). It should be noted however that the WWTP influent P values are relatively low and that further test applications of this technology at WWTPs with higher influent P levels would be required prior to making more definitive conclusions on same.
12. Macroom WWTP discharges up to 800 kg of P to receiving waters annually, through effluent discharge (Irish Water 2020). If it were possible to fully implement this recovery process at the Macroom WWTP, for example, it could lead to up to approximately 500 kg of recovered P product (this is presented for illustrative purposes only with a range of assumptions inherent to the estimate).

13. At a national level it is estimated that approximately 1,475 tonnes of P is discharged annually from Irish municipal WWTPs (O'Donnell et al. 2021), the application of this technology, for example, at a national level would indicate the potential for P-recovery of over 900 tonnes of P (this is presented for illustrative purposes only and acknowledging that there are a wide range of assumptions inherent to the estimate).

5 Life Cycle Assessment – Life Cycle Costs works

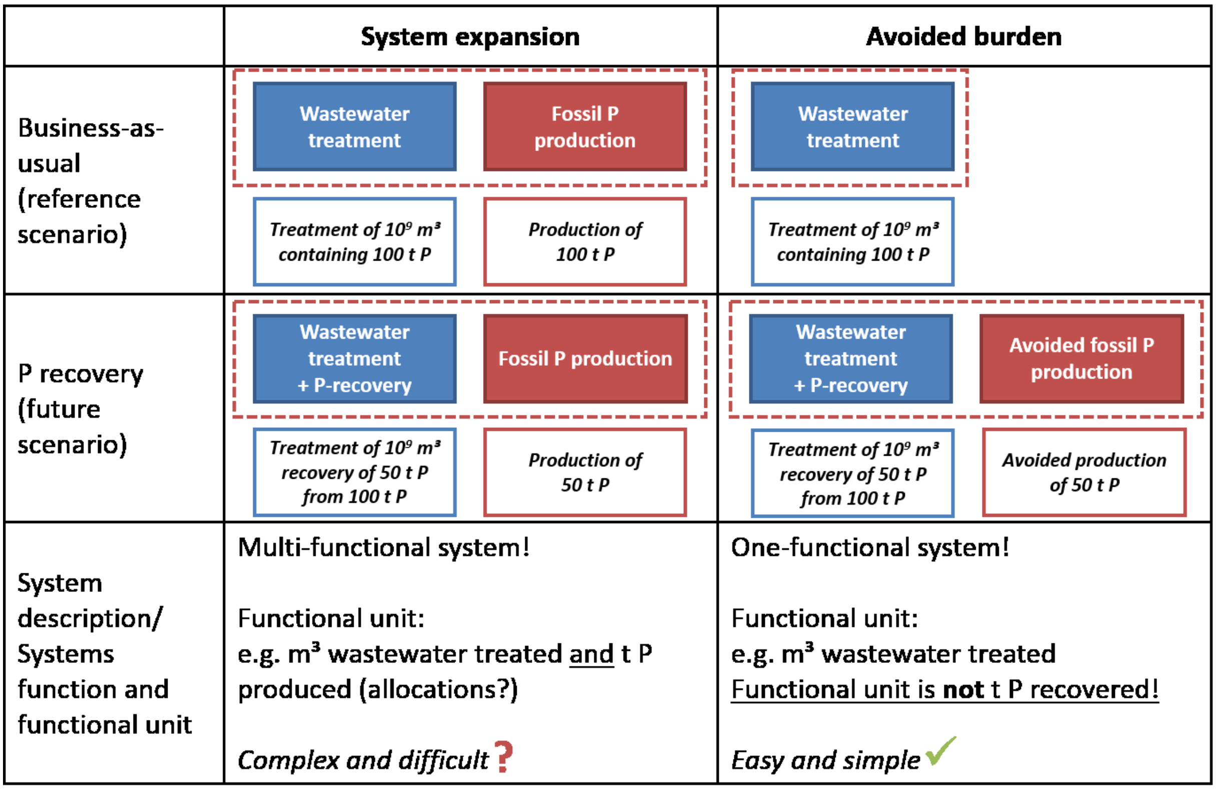
Authors: Gaspard Chantrain Sylvie Groslambert, , Angélique Léonard (ULiège); Anders Nättorp (FHNW)

An environmental analysis was performed on some of the recovery process demonstrators that were larger in scale than the laboratory. The laboratory scale processes were not included in the study to ensure that the data provided was as representative as possible of the industrial scale application. The processes studied therefore include the EuPhoRe®, Struvia™, PARFORCE and PULSE demonstrators. The environmental assessment was done using the life cycle assessment methodology and aim to quantify their environmental impacts. The environmental analysis also allowed to highlight the most impacting steps of each process, this can be used for eco-design purposes. Finally, the environmental performance of each demonstrator was compared with a reference system.

Although very important, legal aspects were not taken into account in the LCA. It was assumed that all products from the project demonstrators were legally usable. In addition, the environmental performance of the demonstrators were compared to the reference system and not to each other. This choice reflects the fact that demonstrators adapt to the needs of particular situations and the legal frameworks of that situation. The demonstrators should therefore be chosen to be most suitable for the situation according to their technical specificity and will therefore not compete in the same situation.

The use of the products from the demonstrators and its consequences were not taken into account in the environmental analysis of this project. The LCA was carried out on the production phases of the P-materials and was therefore called "cradle to gate" LCA.

In the environmental assessment of the demonstrators of the Phos4You project, the first difficulty was to take into account the environmental impacts attributed to the production of the sludge used by the demonstrators. Different approaches are possible to estimate the environmental burden of complex systems. The mains approaches are known as "system expansion" and "avoided burden". They are illustrated in Figure 4.3.1 .



	System expansion	Avoided burden
Business-as-usual (reference scenario)	Wastewater treatment Fossil P production *Treatment of 10^9 m^3 containing 100 t P* *Production of 100 t P*	Wastewater treatment *Treatment of 10^9 m^3 containing 100 t P*
P recovery (future scenario)	Wastewater treatment + P-recovery Fossil P production *Treatment of 10^9 m^3 recovery of 50 t P from 100 t P* *Production of 50 t P*	Wastewater treatment + P-recovery Avoided fossil P production *Treatment of 10^9 m^3 recovery of 50 t P from 100 t P* *Avoided production of 50 t P*
System description/ Systems function and functional unit	Multi-functional system! Functional unit: e.g. m^3 wastewater treated and t P produced (allocations?) *Complex and difficult* ?	One-functional system! Functional unit: e.g. m^3 wastewater treated Functional unit is **not** t P recovered! *Easy and simple* ✓

Figure 4.3.1: System expansion vs. avoided burden (Kraus 2020)

Even if it is presented as more complex or difficult, the "system expansion" approach is chosen in the first place. This choice is explained by the fact that not all the processes use the sludge in the same way and that some demonstrators are integrated directly into the wastewater treatment line and the wastewater treatment plant (WWTP). For instance, Struvia™ is "included" in the process before the sludge dewatering, and EuPhoRe® treats the sludge after its methanisation. The interest in the present case is to allow the combination of the different configurations of the WWTP and to include the sludge processing for P-recovery in a specific way for each process. In addition, the system expansion approach reflects the goal of the project to include phosphorus recovery in the sewage sludge recovery pathway. Nevertheless the "avoided burden" perspective can be considered as a sensitivity analysis and it is realized too. Other approaches are possible such as the attribution of an allocation factor to the WWTP and the "co-products" (treated water, sludge, etc.) for the different parts of the plant (Pradel and Aissani 2019). However, this type of method requires knowledge of specific factors related to each treatment plant, and due to the lack of data it is not possible to apply it in the present project.

5.1 System expansion methodology

Firstly, the system extension approach has been chosen. This consists of studying the environmental performance of a system with two functions. The first is the treatment of wastewater and the treatment of sludge produced during wastewater treatment. In the case of the demonstrators, there will be a recovery of phosphorus from the sewage sludge treatment unlike in the reference system. The second function of the system is the production of phosphorus fertiliser.

5.1.1 Methodological choices

5.1.1.1 *Functional unit*

The functional unit (FU) is defined as 100 m³ of treated wastewater (in the WWTP) (including sludge elimination or valorisation) + 0.80 kg of P_2O_5 fertiliser. We consider only two main functions in the model (wastewater treatment and P-fertiliser production). The amount of P_2O_5 produced and included in the functional unit was calculated in relation to the P_2O_5 concentration typically found in German sewage treatment plants. This concentration is between 6.5 and 7 % of P_2O_5 in the dry matter of the sludge. The quantity of 0.80 kg of P_2O_5 produced as a functional unit was also chosen to reflect the maximum quantity of P_2O_5 recovered out of 100 m³ wastewater with a P-recovery technology (a recovery rate between 95 and 100% of the P_2O_5 present in the sludge is feasible with i.e. the EuPhoRe® process)[1].

In the case of the Phos4You demonstrators, the amount of P is calculated based on the quantity of sludge produced by the treatment of 100 m³ of water, and the specific yield for P recovery of each process.

Depending of the scenario, the "0,80 kg of P_2O_5 " is produced:

- by conventional "chemical" P routes. The reference is the triple super phosphate (TSP) in the reference scenario. This choice is justified by the fact that P-materials are compared to TSP in the quality assessment of the project.
- by the recovery process of Phos4You under study.

---

[1] 0,80 kg of P_2O_5 = 0.82 kg of P_2O_5 x 98.5%. The amount of sludge obtained by the treatment of 100 m³ and after the reduction due to biodigestion is estimated at 60.57 kg DM 20 %. Taking an average of 6.5 to 7 % P_2O_5 in the dry matter of the digested sludge, it is estimated that 0.82 kg P_2O_5 are in the 60.57 kg DM 20 %. Taking into account a recovery rate between 95 and 100 % (maximum achieved for the EuPhoRe® process), the quantity corresponding to the functional unit of 0.80 kg of P_2O_5 is obtained.

The first step of the LCA is the modelling and the evaluation of the impacts of a WWTP, and of the conventional production of P fertiliser (as P_2O_5). They are common to all processes, and they are the reference case.

The study is presented in details in a Master thesis for the grade of Bio-Engineer in Environmental Sciences and Technologies (Chantrain 2021).

Environmental impacts are evaluated with the ReCiPe 2016 method (Huijbregts et al. 2017). Generic data are from Ecoinvent 3.6 database (Wernet et al. 2016), as implemented in Simapro software 9.1 (developed by PRé Consultant in the Netherlands).

5.1.1.2 *Model wastewater treatment plant for the LCA*

The model WWTP is a combination between the plant of Oupeye (Liège, Belgium) and the sludge treatment as commonly practiced in Germany.

The Oupeye plant is considered as representative of a large WWTP. It is processed by AIDE (L' Association Intercommunale pour le Démergement et l'Epuration des communes de la province de Liège) with a capacity of 438,000 PE, coming from nine municipalities around Liège. The sludge treatment is not modelled on the basis of the Oupeye plant but on the basis of the common practice in Germany. The sludge will be therefore processed by a classical bio-methanisation followed by an incineration with energy recovery of the digesta and a landfill of the incineration residues. The sludge treatment path and its modelling will be detailed below.

The Figure 5.1.1 presents the general flowsheet of the WWTP of Oupeye.

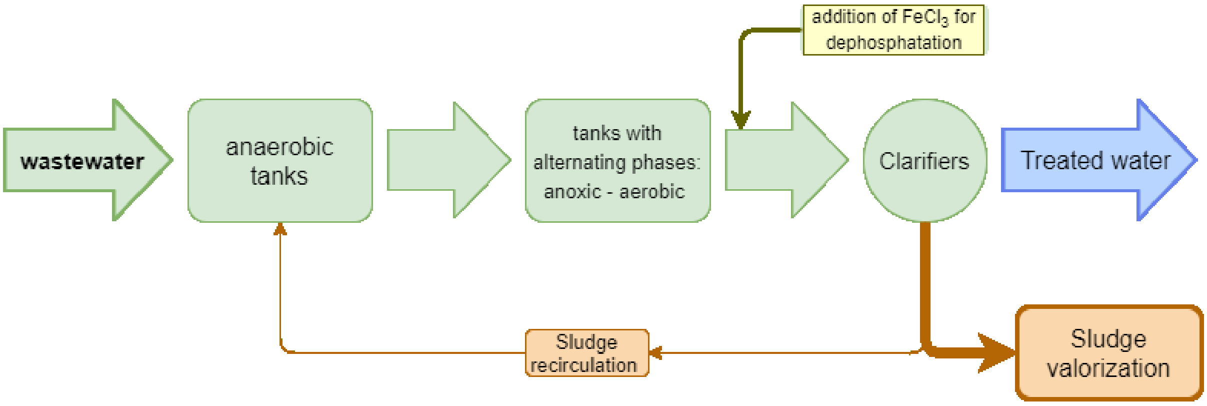


Figure 5.1.1: Flowsheet of the Oupeye WWTP

A small part of the sludge is recirculated in the process but the major part goes for its end-of-life (EoL). The end-of-life pathway modelled corresponds to bio-methanisation of the sludge followed by co-generation (with electricity and heat production) and finally incineration (also with energy recovery). The reference system will be described in more detail further on.

Data for modelling the wastewater treatment plant (chemicals, energy and sludge production) are primary data from AIDE. The waste from grid refusal is incinerated, while the sand from the desanding process is used as fill material. Direct emissions and sludge valorisation impacts are from scientific papers and generic database.

The direct agricultural application of sludge on fields has not been considered in this study, despite the fact that it allows an integral and direct return of phosphorus from the sewage sludge to the fields. This choice is motivated by the fact that the standards in terms of trace pollutants for agricultural spreading exclude a large number of sludges produced. In addition, the legislation for this practice is becoming more and more restrictive. It is already forbidden in several European countries such as Germany, the Netherlands or in Switzerland. The hypothesis made here is that agricultural spreading is not possible for legislative reasons and that phosphorus recovery processes are used to ensure the return of phosphorus from sludge to the fields.

5.1.1.3 *Conventional route for P-fertiliser production*

Conventional phosphorus fertiliser production is modelled by the production of triple super phosphate (TSP). This choice is motivated by the fact that the properties of the phosphorus fertilisers from the demonstrators were compared with those of TSP in the quality assessments works achieved within the Phos4You project.

It was shown in the quality assessments of the P-materials from the demonstrators that the phosphorus they contained was at least as available for plants as that in the TSP after a number of cuts (usually 4) in pot trials (Bogdan et al. 2021). A unit equivalence factor was therefore chosen between the amount of P_2O_5 contained in the P-materials and that contained in the TSP. In view of the good results on the bioavailability of phosphorus in the P-materials of the demonstrators, this unit equivalence factor appears to be prudent. In addition, some forms of phosphorus allow a slow release of P into the soil, which is known to reduce eutrophication and allow better utilisation of P by plants (Shaviv and Mikkelsen 1993). These advantages will not be taken into account in the environmental analysis of P-materials.

The environmental impacts of TSP production were modelled using the corresponding entry in the generic Ecoinvent database. This entry includes all the stages of TSP production, starting from the extraction of phosphate rock.

5.1.1.4 *Multifunctional systems – scenario description*

The different scenarios for the multifunctional systems are briefly presented in Table 5.1.1. The boundaries of each system and the calculations involved will be explained in more details in each of the chapters dedicated to them.

As specified in 5.1.1.1, the functional unit (FU) is the treatment of 100 m³ of wastewater and the production of 0,80 kg of P_2O_5.

The treatment of 100 m³ of wastewater produces a certain amount of sludge, depending of the configuration of the WWTP. From this sludge, some P_2O_5 is recovered, with a yield depending of the process. Therefore, the "0,80 kg P_2O_5" of the FU is distributed between the P_2O_5 recovered with the Phos4You demonstrator and the necessary complement of conventional chemical production (noted as "chemical P") to reach the desired quantity (0,80 kg). As a reminder, the amount of 0.80 kg P_2O_5 was calculated based on the typical concentration of German sewage sludge and the highest recovery rate among the studied demonstrators. Table 5.1.1 summarizes the system expansion approach applied to each demonstrator as well as the estimated recovery percentage with the calculation assumptions explained earlier.

For the reference scenario, the EoL of the sludge considered starts with a bio-methanisation of the sludge (with cogeneration of the biogas produced). The digested sludge is then incinerated with energy recovery and the incineration residues are landfilled.

The electricity used in all the systems studied was modelled using the 2016 German electricity mix. The influence of this modelling choice will be investigated later by means of a sensitivity analysis of the origin of the electricity used.

It is also important to note that only phosphorus is taken into account in the LCA of the P-materials from demonstrators and that the calculations to determine the equivalence between the different forms of phosphorus found in the P-materials are based on stoichiometry. Finally, it must also be considered that the environmental analysis here focuses on the phosphorus content of the P-materials and that other nutrients may be present in the products from the demonstrators.

Table 5.1.1: Scenarios for the multifunctional systems

System	Origin of the P_2O_5	Sludge treatment	Estimated recovery percentage
WWTP + EuPhoRe®	0.79 kg P_2O_5 from EuPhoRe® + 0.01 kg "chemical P"	Sludge treated as in EuPhoRe® process (see demonstrator I1)	96.3 %
WWTP + Struvia™	0.26 kg P_2O_5 from Struvia™ + 0.54 kg "chemical P"	Sludge treated as in Struvia™ process (see demonstrator I6.1)	34.7 %
WWTP + PARFORCE	0.54 kg P_2O_5 from PARFORCE + 0.26 kg "chemical P"	Sludge treated as in PARFORCE process (see demonstrator I2)	65.9 %
WWTP + Pulse	0.72 kg P_2O_5 from Pulse + 0.08 kg "chemical P"	Sludge treated as in Pulse process (see demonstrator I3)	87.8 %
WWTP + conventional chemical production	0.80 kg of P_2O_5 "chemical P"	Incineration for energy valorisation	0 %

The details of the calculations leading to the values in the table above will be explained in the system explanation of each demonstrator. The general principle is that the P_2O_5 quantities are obtained from the data of the demonstrators by relating the quantities of P_2O_5 produced by the demonstrators to the quantity of sludge treated by the demonstrators and by linking this quantity of P_2O_5 to the quantity of sludge produced by the treatment of 100 m³ of wastewater. This amount of sludge was estimated to be 305.6 kg of raw sludge at DM 5% for the Oupeye WWTP. The same amount of sludge is treated by the different demonstrators by being integrated in a system. The system studied for each demonstrator will be detailed below. The assumption made here is that the phosphorus content of the sludge used by the demonstrators is similar to the one of the standard German sludges (between 6.5 and 7 % P_2O_5 in the dry matter of the digested sludge). This assumption was verified by data provided by the operators of the EuPhoRe®, PARFORCE and PULSE demonstrators. For the Struvia™ process, the P-content was estimated by taking into account the fact that the sludge used was not digested, which lowered the P_2O_5 content to 4.9 % of dry matter. The sludge volume reduction by biodigestion was calculated by taking into account an organic matter rate of 50 % of the sludge dry matter and a degradation rate of 45 % of the sludge organic matter.

Discrepancies between the recovery rates calculated on the basis of the assumptions used in the LCA and the actual recovery rates of the demonstrators can be explained by the fact that the sludge used in the data collection may have had a different phosphorus content or by the fact that the recovery technologies were not yet at a sufficiently advanced stage of development to achieve the final recovery rate.

5.1.1.5 *Selection of impact categories studied*

As said above (5.1.1.1), the environmental assessment of the project uses the ReCiPe 2016 method (Huijbregts et al. 2017) and the generic data are taken from the Ecoinvent 3.6 database (Wernet et al. 2016). The entire project is implemented in Simapro 9.1 software (developed by PRé Consultant in The Netherlands).

The 2016 ReCiPe methodology proposes a set of 18 impact categories. These categories are: global warming, stratospheric ozone depletion, ionizing radiation, ozone formation (human health), fine particulate matter formation, ozone formation (terrestrial ecosystems), terrestrial acidification, freshwater eutrophication, terrestrial ecotoxicity, freshwater ecotoxicity, marine ecotoxicity, human carcinogenic toxicity, human non-carcinogenic toxicity, marine eutrophication, land use, mineral resource scarcity, water consumption.

In order to synthesise the results, certain impact categories were selected in the rest of the project. This selection was done in three steps and based on the results of the reference system for the system expansion method (developed below). The first step was the exclusion of the toxicity categories due to the large uncertainty associated with these categories and their lack of relevance to the nature of the project. The selection of categories was then based on the results of the normalisations. Normalisation allows the impacts on the different categories to be ranked by dividing the impacts by a common reference value. In the case of the ReCiPe 2016 method, this common value is the average pollution generated per person worldwide in 2010.

Figure 5.1.2 shows the results of the normalisation of the reference system impacts of the expansion system method.

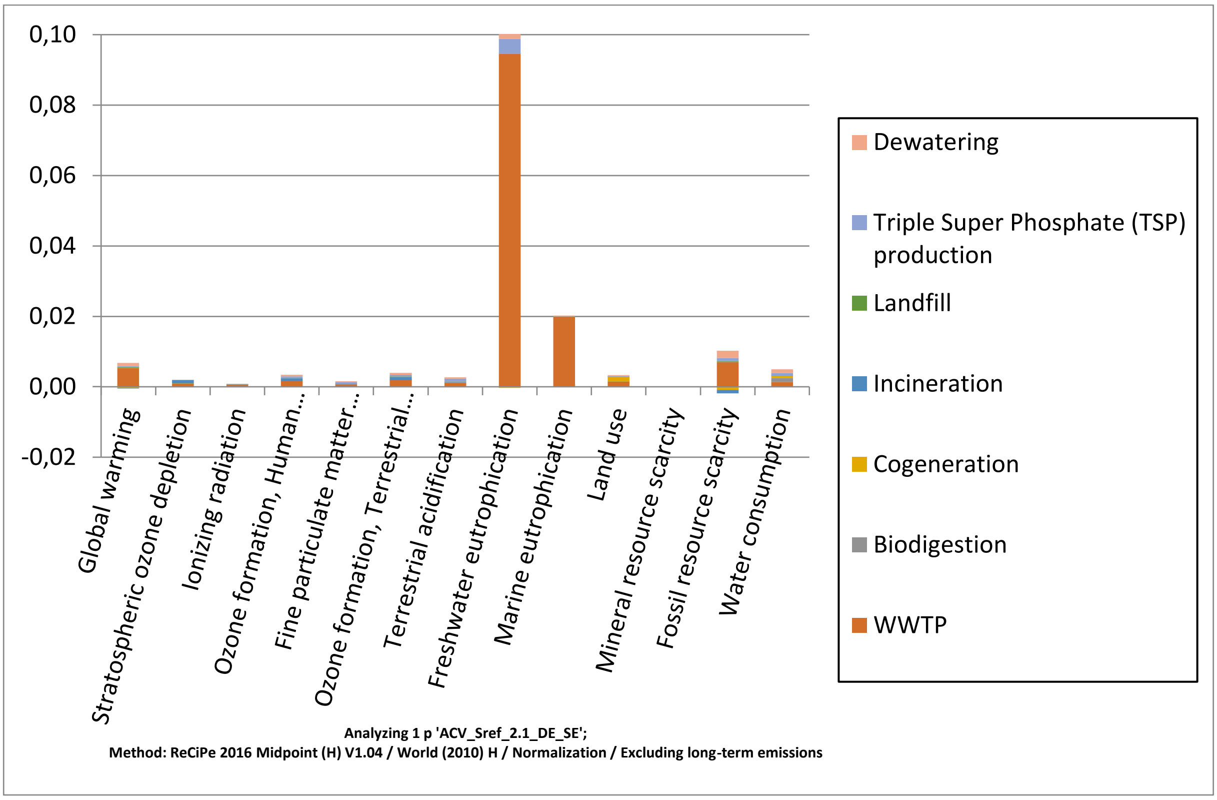


Figure 5.1.2: Results of the normalisation of the reference system impacts of the expansion system method: ReCiPe 2016 Midpoint (H) V1.04 / World (2010) H / Normalisation / Excluding long-term emissions

Based on these results and their relevance to the project, the categories of global warming, freshwater as well as marine eutrophication and fossil resource scarcity were selected. Finally, despite its low normalisation score, the mineral resource scarcity category was selected given the relevance of such a category in a project aiming at recycling a mineral material such as phosphorus.

5.1.2 Results for four recovery processes

In the subsequent part, the systems studied will first be described and then the main results of the environmental analysis will be presented for each system, according to the selected impact categories.

5.1.2.1 *LCA of the reference system*

The reference case includes the wastewater treatment plant with the energy consumption (electricity and fuel), the chemicals consumption and the emissions (mainly to air) of the WWTP. The treatment of plant waste (grid refusals and sand removal) is also taken into account.

The WWTP produces undigested sludge. In this scenario it is sent directly to a biodigestion unit. The consumption of this digestion (electricity and heat) and the emissions (leakages) are also considered. During this biodigestion, the organic matter content decreases, which significantly reduces the amount of sludge. A degradation of 45 % of the organic matter is taken into account to produce biogas which will be used in a co-generation unit to produce heat and electricity. Also here, the emissions as well as the energy (heat, electricity) and reagent consumption have been taken into account. The heat and electricity produced in the cogeneration process are included as avoided products. The cogeneration efficiencies taken into account are 37 % for electricity production and 52 % for heat recovery (Jungbluth et al. 2007).

The dewatering of digested sludge is then planned according to an average of available techniques (including electricity and reagent consumption). The last two stages of sludge treatment are the incineration with recovery of heat (and electricity) and extraction of fly ash and landfilling of incineration residues. All these steps were taken into account using data from the Ecoinvent database. The recovery efficiencies adopted for the incineration phase are those from the Ecoinvent database and are 52 % for heat recovery and only 1.6 % for net electricity production (Jungbluth et al. 2007).

Phosphorus fertilizer production has been taken into account through the Ecoinvent entry for TSP production. This entry contains all the production stages with their consumption and emissions. The amount of P_2O_5 produced in this system is 0.8 kg which is equivalent to 1.66 kg of TSP at 48 % de P_2O_5.

The Figure 5.1.3 shows the boundaries of the reference system.

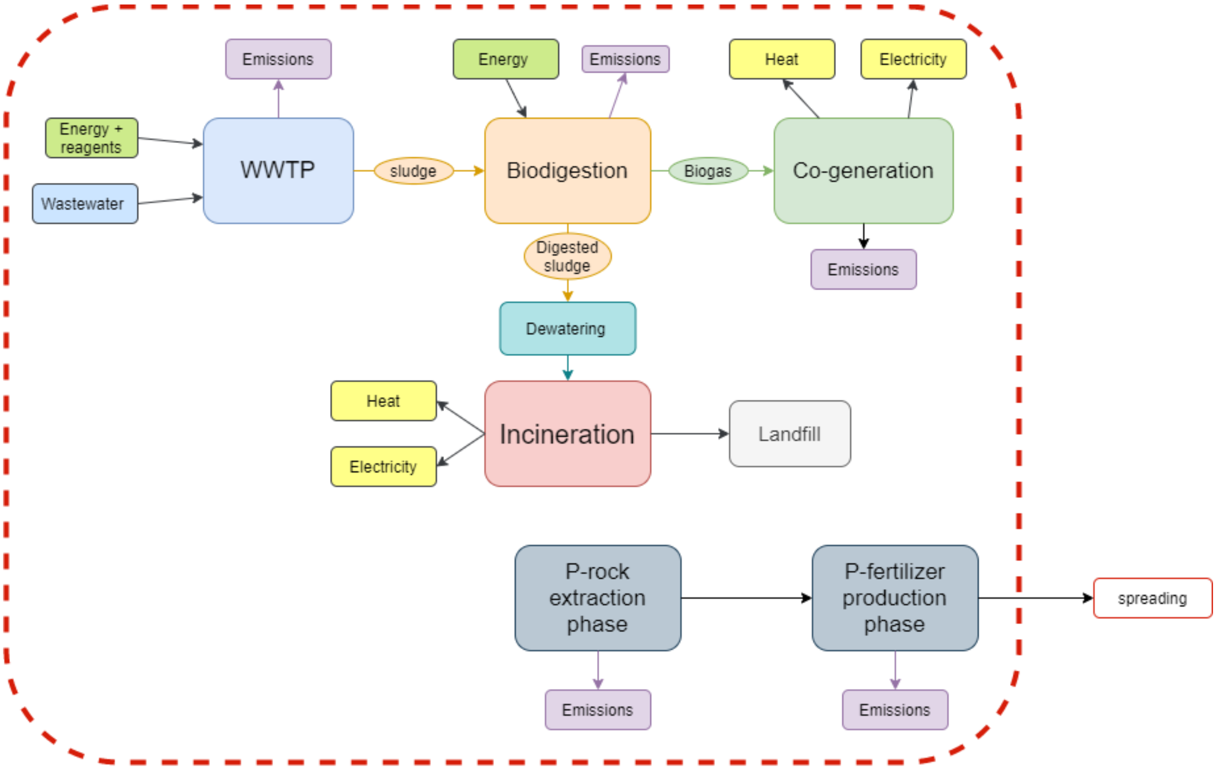


Figure 5.1.3: Boundaries for the reference system: 100 m³ of wastewater treated in the WWTP and 0.80 kg of P_2O_5 by chemical route

The Figure 5.1.4 shows the impact of the multifunctional reference system. Except in the mineral resource scarcity category, the WWTP is the impacting part of the system.

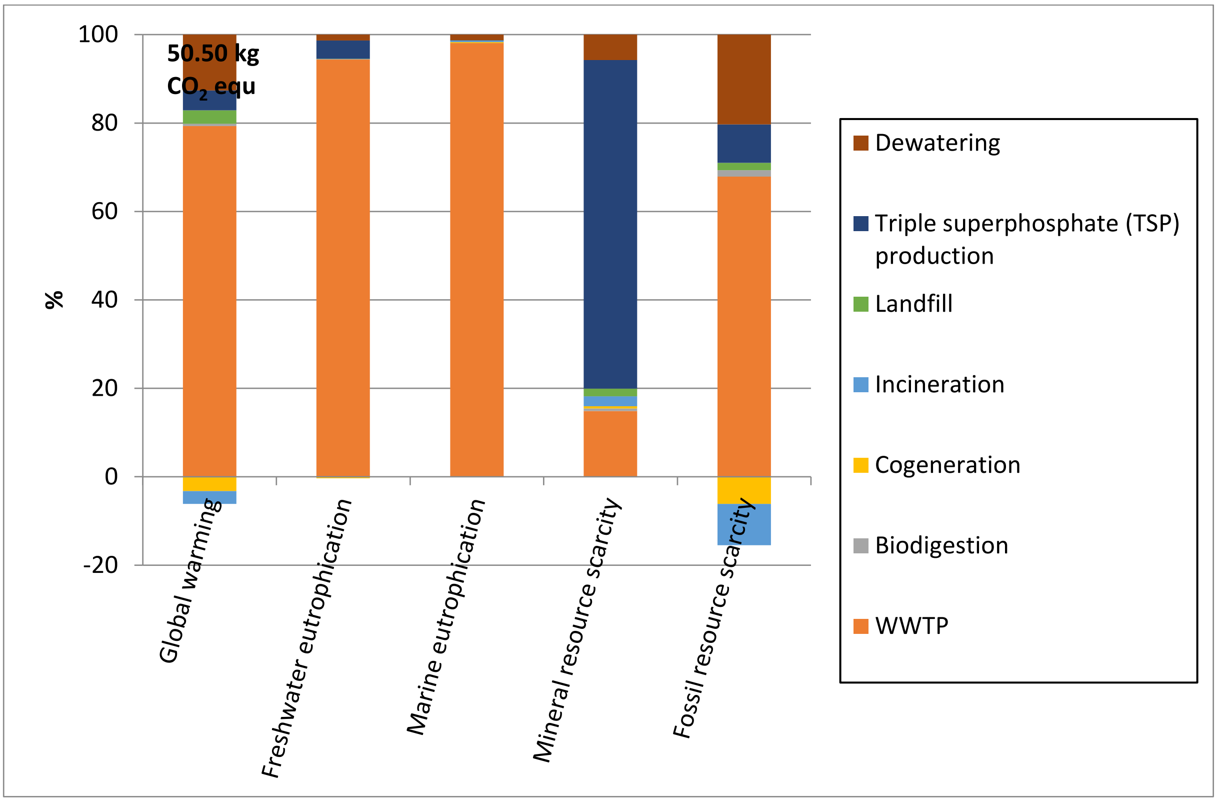


Figure 5.1.4: Environmental impacts of the multifunctional system including 100 m³ of treated water in the WWTP, and 0,80 kg of chemical P_2O_5 – Characterisation ReCiPe 2016 H/World H

As can be seen in the graph above, the wastewater treatment plant is responsible for most of the environmental impacts of the system (in orange). The beneficial impacts of cogeneration (yellow) and incineration (blue) are also visible. The dewatering phase (brown) is responsible for the negative environmental impacts due to the consumption of electricity and reagents. Finally, TSP production (dark blue) generally has a rather small effect on the categories studied, except for the category of mineral resource depletion, which was expected.

5.1.2.2 *LCA of the EuPhoRe® system*

The EuPhoRe® process is a thermo-chemical process for the production of phosphorus-rich sewage sludge ashes (SSA) with a content of approximately 16 % P_2O_5. This process is described in the chapter on this process and is represented in the Figure 3.2.1.

The multifunctional system including the EuPhoRe® process is similar to the reference system explained above by replacing incineration and landfill of residues with the EuPhoRe® process and the production of P-rich SSA. This process also allows for significant heat recovery.

In this system as for the reference system, the treatment of 100 m³ of water produces 305.6 kg DM 5 % of non-digested sludge which corresponds after digestion and dewatering to 60.57 kg of DM 20 % sludge. The reduction of dry matter following biodigestion is calculated on the basis of an organic matter rate of 40 % of the dry matter and a degradation of 45 % of the total organic matter. The 60.57 kg DM 20% sludge is then dried in a solar greenhouse to reach a dry matter content of more than 75 %. Using the annual P-rich SSA production data and annual sludge consumption, it was calculated that 0.79 kg of P_2O_5 was produced from the 60.57 kg of sludge at DM 20 %. The main data can be summarised by knowing that the process treats 5,200 tonnes of sludge per year, which allows the production of 1,590 tonnes of P-rich SSA, which contains 254.4 tonnes of P_2O_5. The sludge is pre-treated by a solar dryer before entering the process and the amount of heat recovered is 9,100 MWh per year. The implicit assumption here is that the composition of the sludge used by the EuPhoRe® process is similar to the sludge produced by the studied WWTP after biodigestion.

For the multifunctional system, the sludge resulting of the 100 m³ of wastewater treated in the WWTP can deliver 0.79 kg of P_2O_5 equivalent in the P-rich SSA material; 0.01 kg of P_2O_5 fertiliser have to be produced by conventional chemical route to reach the "0.80 kg P_2O_5 " objective of the FU. This 0.01 kg of chemically produced P_2O_5 corresponds to the production of 0.0208 kg of TSP at 48 % P_2O_5.

The system boundaries for the EuPhoRe® process are presented in Figure 5.1.5.

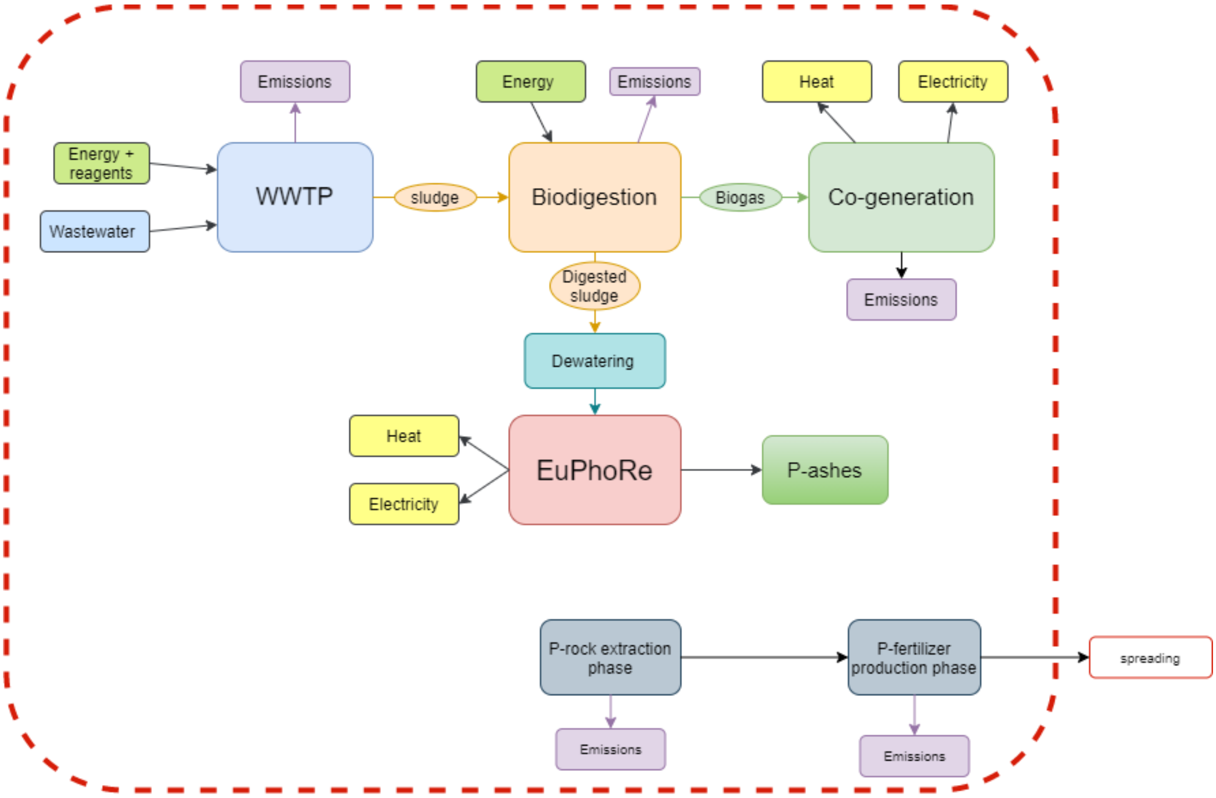


Figure 5.1.5: System boundaries for the EuPhoRe® process in the multifunctional system

The Figure 5.1.6 shows the impacts of the different parts. The WWTP (orange) is the main impacting step in all categories. The environmental benefits of the EuPhoRe® process (light blue), that can be seen in the global warming and the fossil resources scarcity categories, are due to the heat recovery. The sludge dewatering stage (brwon) is also responsible for adverse environmental effects, while cogeneration (yellow) is responsible for beneficial effects in general.

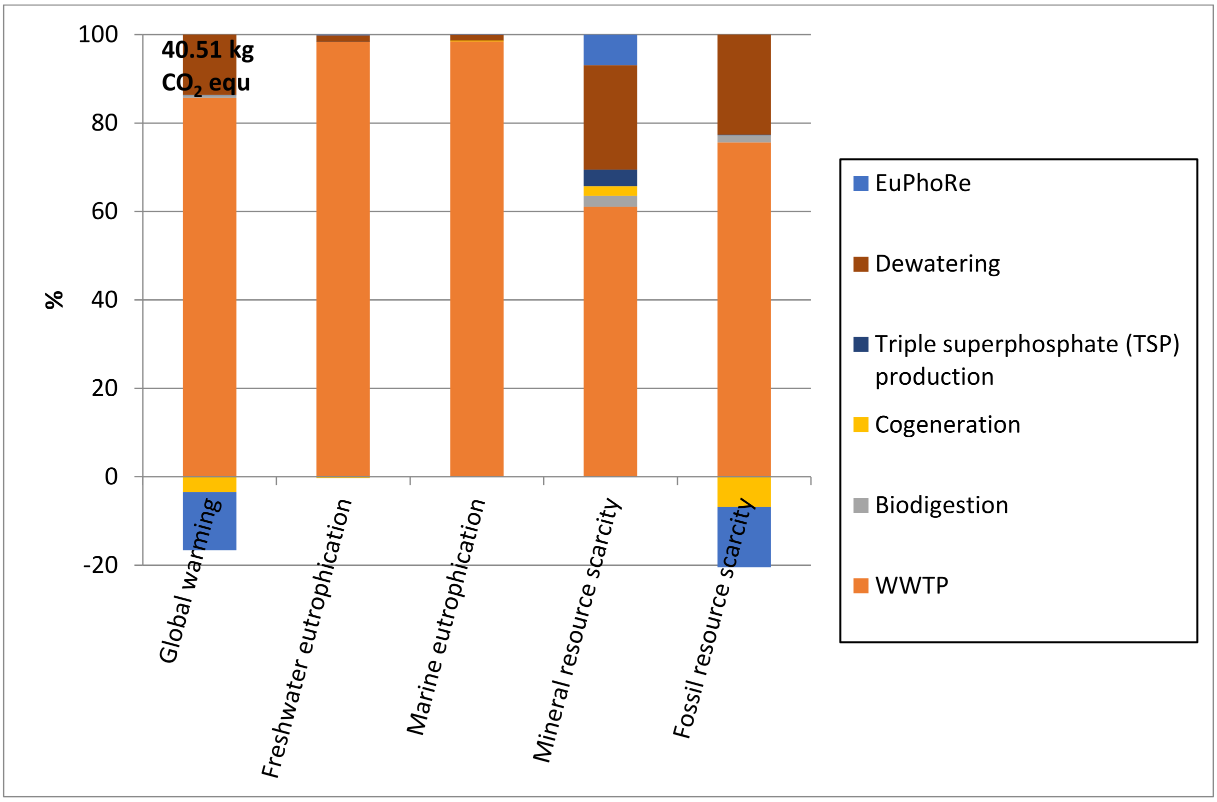


Figure 5.1.6: Environmental impacts of the multifunctional system including 100 m³ of treated water in the WWTP, the P recovery from the sewage sludge in EuPhoRe® process and the additional production of chemical P to obtain 0,80 kg of P_2O_5 – Characterisation ReCiPe 2016 H/World H

It is also interesting to study the environmental impacts of the recovery process alone in order to identify the most impactful steps of the process. To do so, another environmental assessment was performed on the production of 1 kg of P_2O_5 by the process. In this case, only the consumption of the process is taken into account (energy and reagents), the sludge is therefore considered free from an environmental point of view.

The Figure 5.8 shows the details of the EuPhoRe® process, for the production of 1 kg P_2O_5 equivalent as SSA. The large benefit from the heat recovery (in light orange) is obvious in all impact categories. The negative effects on the environment come mainly from the use of electricity (green), sodium bicarbonate (brown) and magnesium chloride (yellow). It is important to note that the beneficial effect of heat production can only be taken into account if the heat is actually used by a third-party user, and therefore substitutes the use of another heat source.

Given the importance of the environmental benefit of recovered heat, it is important from an environmental point of view to optimise this recovery. The majority of the deleterious effects on the environment are caused by the use of electricity, which shows the importance of minimising this consumption. The use of reagents such as sodium bicarbonate and magnesium chloride should also be optimised according to the composition and quantity of incoming sludge, if not already done.

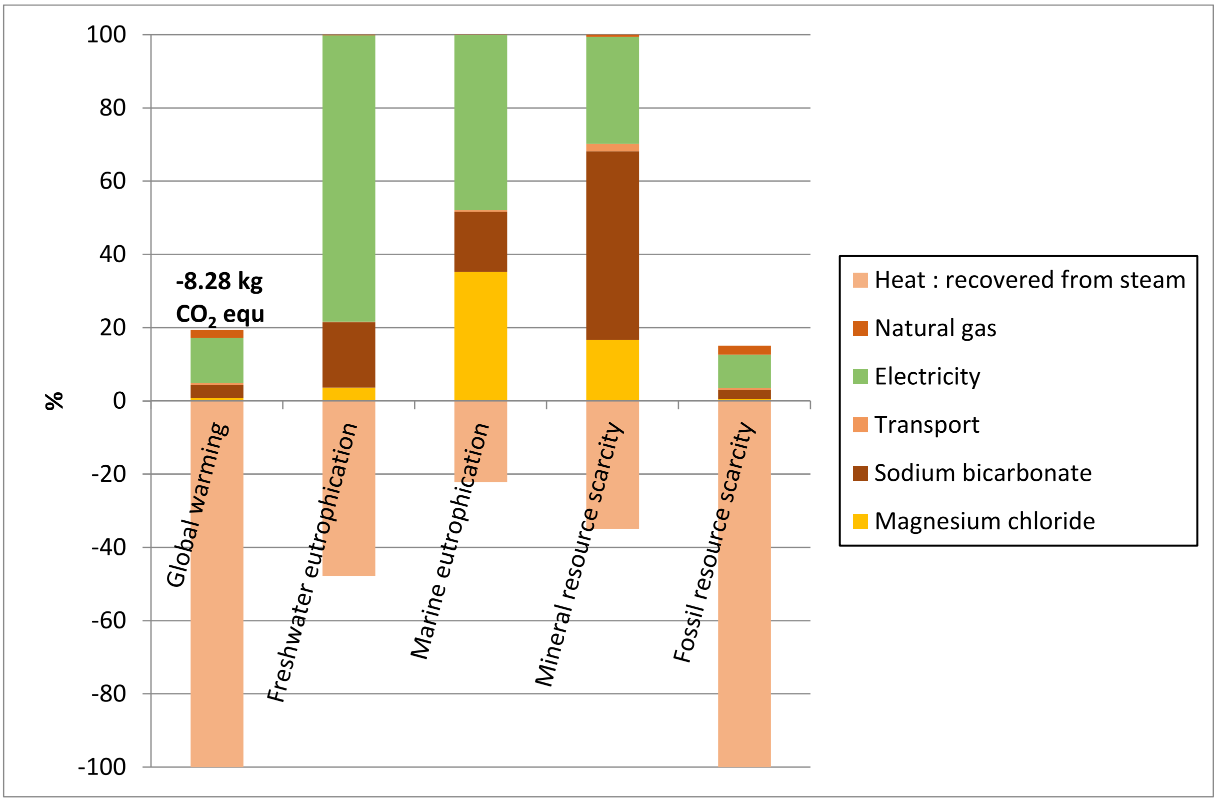


Figure 5.1.7: Environmental impacts of the production of 1 kg of P_2O_5 by EuPhoRe® process – Characterisation ReCiPe 2016 H/World H

Figure 5.1.8 shows the comparison of the environmental impacts of the EuPhoRe® system and the reference system.

The impacts of the EuPhoRe® system are overall lower, especially in the categories of mineral and fossil resource depletion and global warming. The difference in impacts on the mineral resource depletion category is due to the significant production of P_2O_5 by the EuPhoRe® process (which has a recovery rate of about 95 to 99 % of the P contained in the digested and dried sewage sludge).

In order to draw conclusions, it is important to consider the significance of the differences in impacts. To do so, the conclusions of (Jolliet et al. 2015) will be used as well as a quick uncertainty analysis performed with the Simapro tool provided for this purpose. Based on these two elements, the differences of more than 10 % are considered significant for the global warming and fossil fuel depletion categories, while a difference of 30% is required for the eutrophication categories. Based on the Simapro uncertainty analysis, a difference of less than 30 % for the mineral resource scarcity category will be considered non-significant.

It is apparent that the differences in impacts on the categories of climate change, fossil and mineral resources scarcity are significant. This comparison clearly indicates the advantage of the EuPhoRe® system from an environmental point of view.

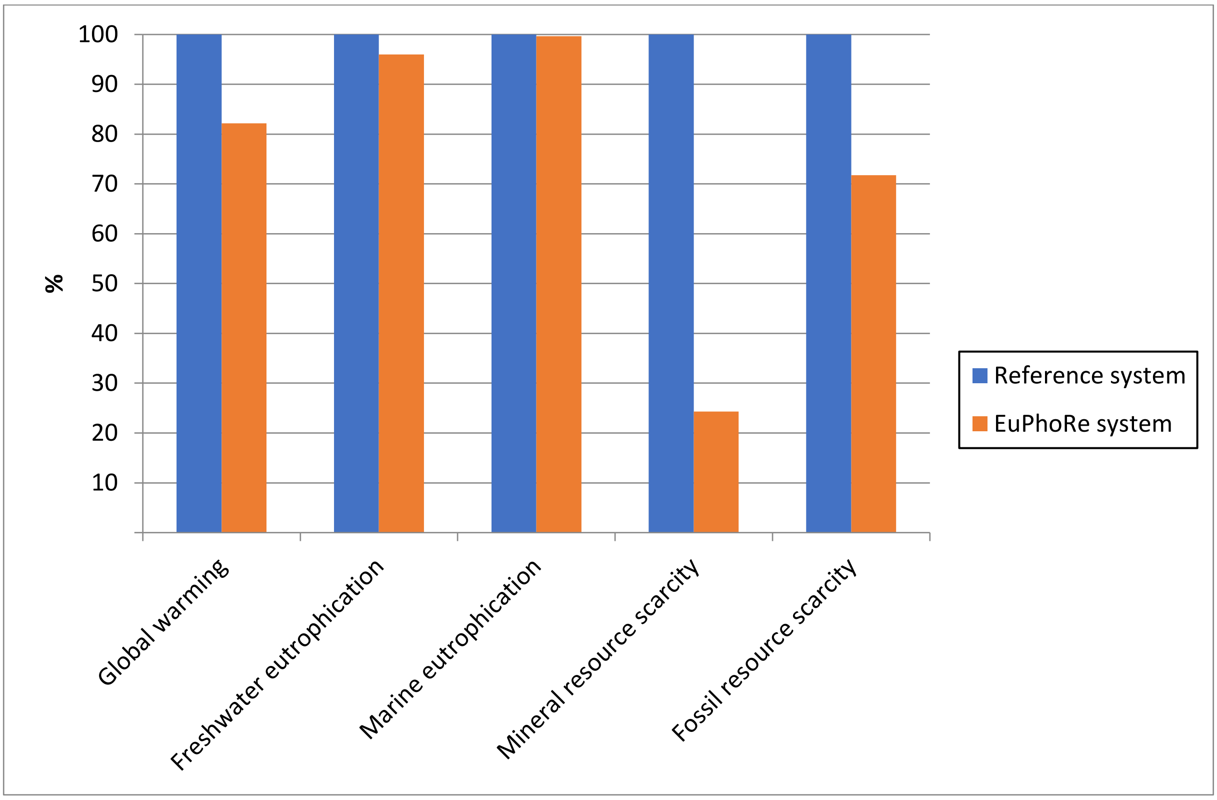


Figure 5.1.8: Comparison of the EuPhoRe® system and the reference system in terms of environmental performance– Characterisation ReCiPe 2016 H/World H

5.1.2.3 *LCA of the Struvia™ system*

The Struvia™ process is integrated directly into the wastewater treatment plant and treats unthickened sludge (DM 5%). This process combines bio-acidification with struvite precipitation. The bio-acidification is done by adding co-substrate easily degradable in anaerobic phase. The addition of the co-substrate allows the release of P in solution and the development of acidifying bacteria which lowers the pH of the solution and thus allows the maintenance of phosphorus in solution. The phosphorus will then be precipitated to obtain hydroxyapatite (HAP). The resulting product is a mix of hydroxyapatite (HAP) $Ca_5(PO_4)_3.OH$, $CaCO_3$ and iron (Fe) in trace. The phosphorus level of the final product is 6 and 8 % of P for the dry product, corresponding to 14-18 % of P_2O_5. This value can vary depending on the sludge that is fed in the process. The final product will be exported as a dewatered form with 35-50 % dry matter. Here, the average values of 16 % P_2O_5 and 43 % DM were used for the calculations. A metal extraction system, OPALIX, is available depending on the composition of the treated water but is not installed on the pilot studied here.

This process has been implemented in two pilots with different capacities, the first one has a capacity of 103 m^3 of DM 5% sludge per day and the second of 4 m^3 per day. Data are based on the pilot operating with a flow rate of 103 m^3 of sludge per day. It is located in Tergnier. The pilot of 103 m^3 sludge/day can produce around 1.3 tonne/day of HAP product (43 % DM).

The data from the two pilots are similar in terms of reagent consumption, but the electrical consumption of the small-scale pilot is significantly higher (10 kWh/m^3 instead of 3 kWh/m^3). Electricity consumption is modelled by the German low voltage electricity mix of 2016.

The co-substrate used for the bio acidification is a waste, produced locally (50 km). It is a residue of sugar from candied fruit or molasses production. It is a "real waste" that has to be disposed from production sites. Therefore, it is "free" of burden on an environmental point of view.

The polymer powder used is an anionic flocculant and is modelled using the corresponding Ecoinvent entry (polyacrylamide).

The Figure 5.1.9 shows the Struvia™ process.

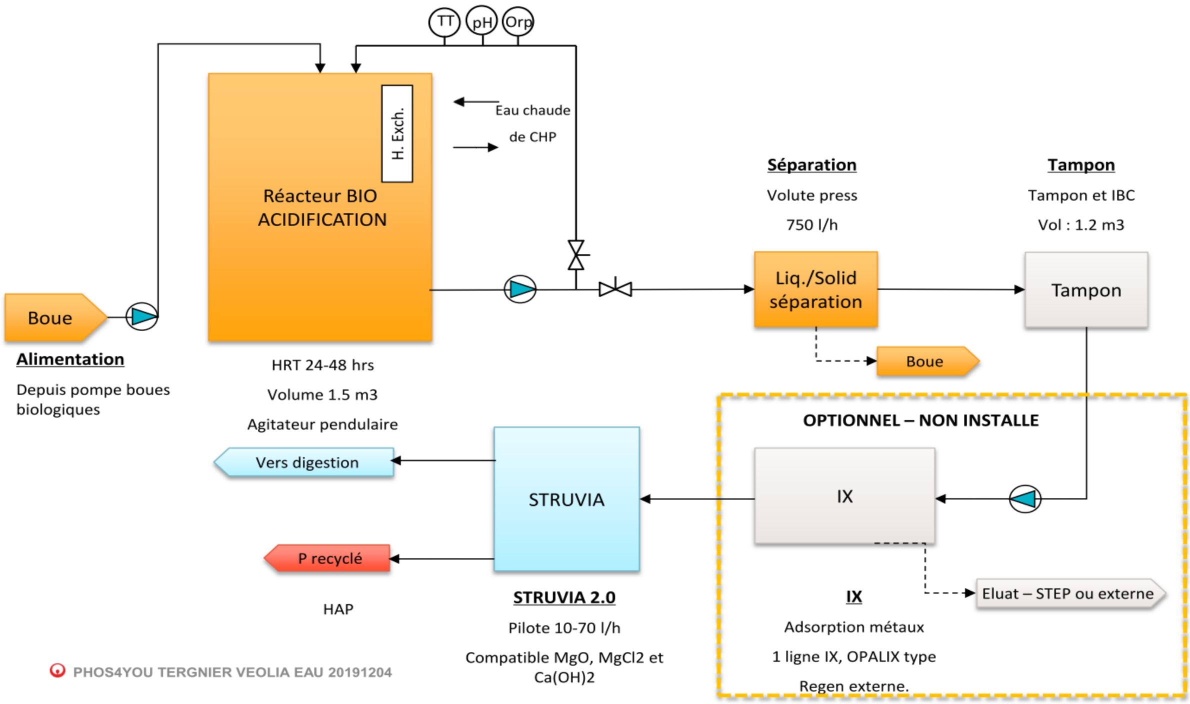


Figure 5.1.9: Tergnier pilot plant of the Struvia™ process – the OPALIX part is not installed (Veolia 2019)

The WWTP model is modified to include the Struvia™ process before the sludge dewatering. The Struvia™ process includes the dewatering of the final product (with addition of polymer etc.).

For the multifunctional system, the sludge resulting of the 100 m³ of wastewater treated in the WWTP can deliver 0.26 kg of P_2O_5 equivalent in the P-material; 0.54 kg of P_2O_5 fertiliser have to be produced by conventional chemical route to reach the "0.80 kg P_2O_5" objective of the FU. This corresponds to a production of 1.12 kg of TSP per chemical route. The amount of 0.26 kg P_2O_5 produced by the Struvia™ process was obtained from the daily production of P_2O_5 and the daily consumption of sludge at DM 5%. It was estimated that the Struvia™ process could produce 0.26 kg P_2O_5 from the 305.6 kg DM 5% sludge generated during the treatment of 100 m³ of water.

The system including the Struvia™ process is broadly identical to the reference system with the inclusion of the Struvia™ process after the WWTP. The Struvia™ process also has the effect of increasing the organic matter in the sludge by adding an organic co-product which will be degraded to 95% in the biodigestion phase. The increase in biogas production due to this additional degradation has also been taken into account.

The system boundaries for the Struvia™ process are presented in Figure 5.1.10.

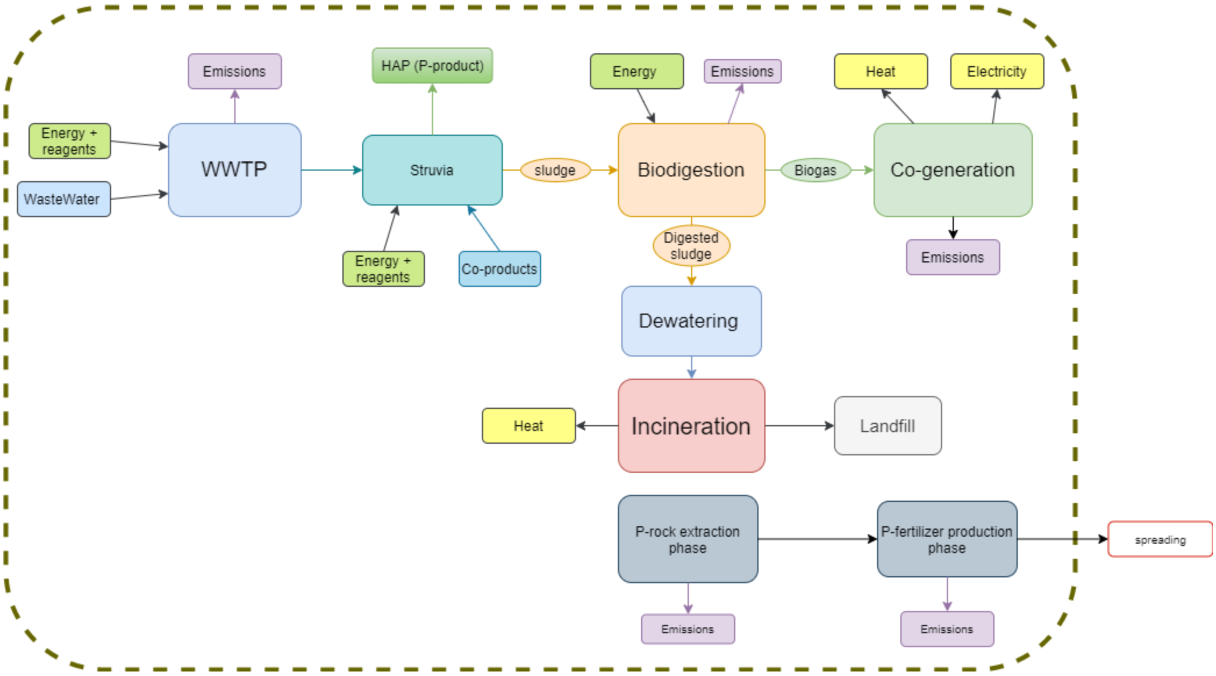


Figure 5.1.10: System boundaries for the Struvia™ process in the multifunctional system

The Figure 5.1.11 shows the impacts of the different parts. The WWTP (orange) is the main impacting step in all categories, except mineral resource scarcity where it is the chemical phosphorus fertiliser production. The beneficial effect of cogeneration (in yeloow) is also clearly visible.

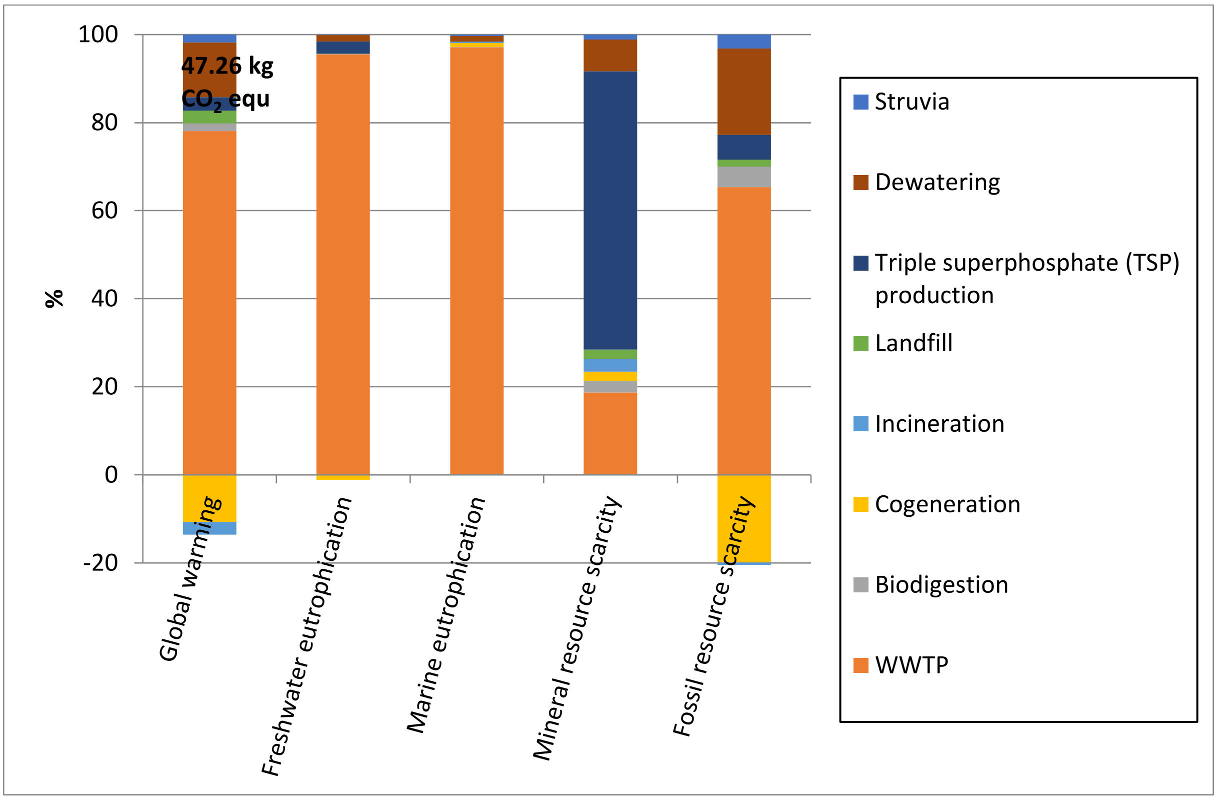


Figure 5.1.11: Environmental impacts of the multifunctional system including 100 m³ of treated water in the WWTP, the P recovery from the sewage sludge in Struvia™ process and the additional production of chemical P to obtain 0.80 kg of P_2O_5– Characterisation ReCiPe 2016 H/World H

As for the EuPhoRe® process, the environmental impacts of the production of 1 kg of P_2O_5 by the Struvia™ process will be evaluated. The Figure 5.1.12 details those impacts. The evaluation here focuses only on the electricity and reagent consumption of the Struvia™ process to supply 1 kg of P_2O_5. The environmental impacts of the sludge production are not taken into account, so it is considered as free of environmental impact. The polymers used for the flocculation and the electricity (DE) have the major impacts on the process.

Given the importance of the impacts caused by electricity consumption (green), it would be interesting to verify that this cannot be reduced. The same applies to the consumption of polymers (yellow). The optimisation of the dewatering stage of the final product (using electricity and polymers) should therefore be investigated.

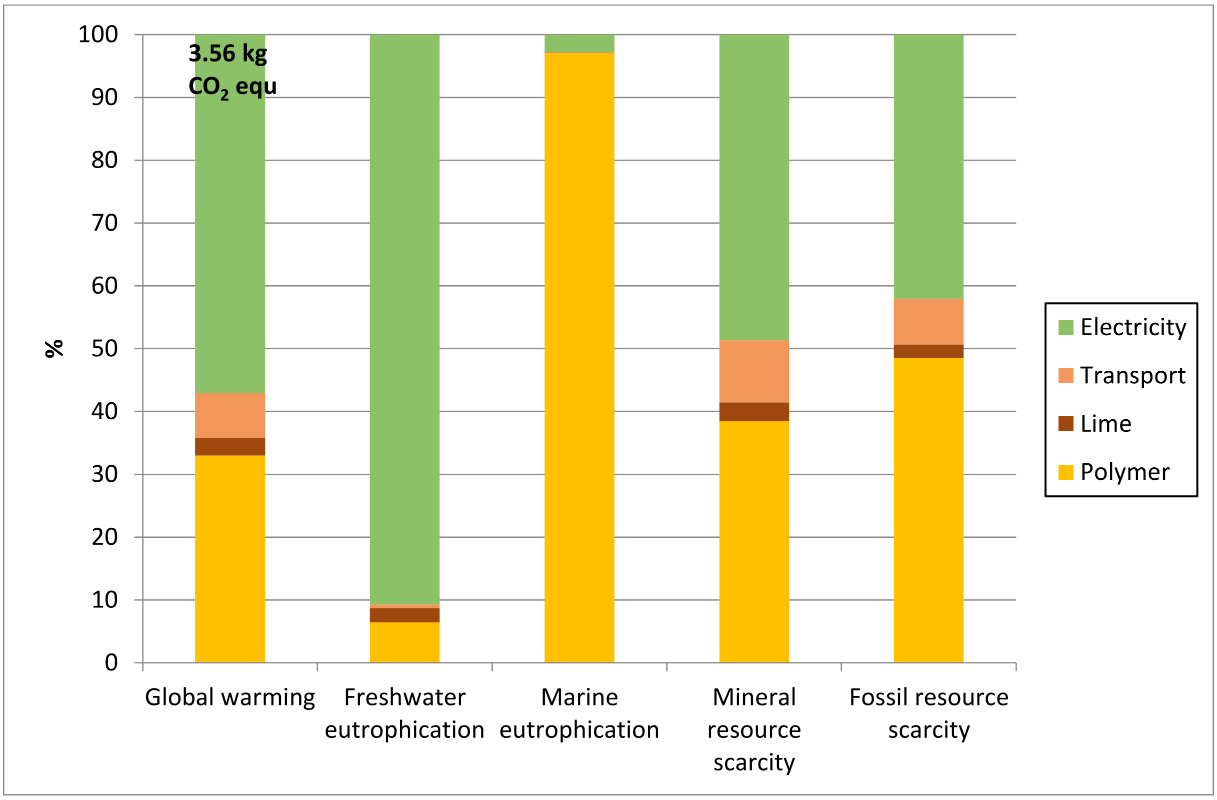


Figure 5.1.12: Environmental impacts of the production of 1 kg of P_2O_5 by Struvia™ process– Characterisation ReCiPe 2016 H/World H

Figure 5.1.13 shows the comparison of the environmental impacts of the Struvia™ system and the reference system. The impacts of the Struvia™ system appear to be slightly lower than those of the reference system for the categories of fossil fuel depletion and global warming. These deviations can be considered significant given that they exceed the required 10% in these categories (Jolliet et al. 2015). The impact of the Struvia™ system on the mineral resource depletion category is lower than the impact of the reference system on this category. This is due to the recovery of phosphorus by the Struvia™ process, which allows the substitution of part of the TSP production and thus reduces the use of phosphate rock. However, a difference of 30 % is required in order to consider the differences in impacts on the mineral resource scarcity category as significant, so the difference observed here will not be considered as such. The same is true for the difference observed on the climate change category which is also below the significance level (of 10% for this category). Only the difference in the fossil fuel depletion category will therefore be considered significant.

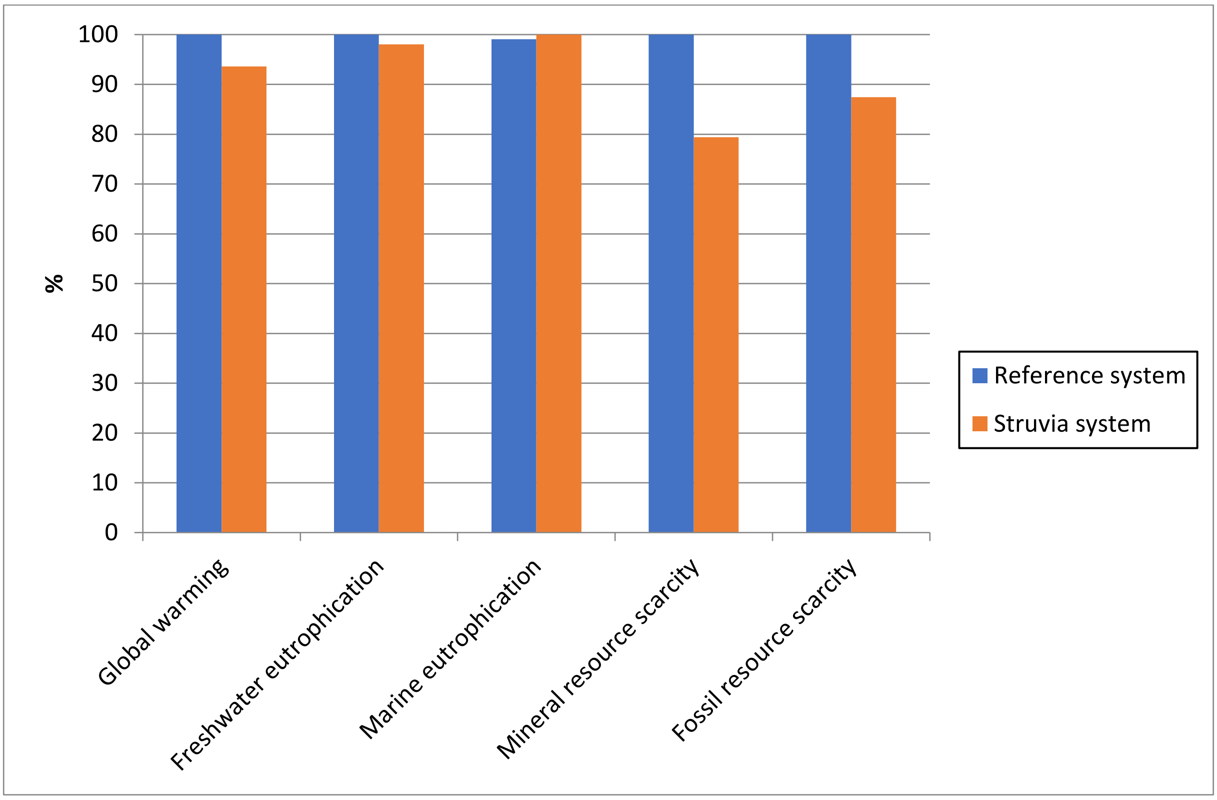


Figure 5.1.13: Comparison of the environmental impacts of the Struvia™ system and the reference system– Characterisation ReCiPe 2016 H/World H

5.1.2.4 *LCA of the PARFORCE system*

The PARFORCE chemical process allows the recovery of phosphorus from incineration ash in the form of phosphoric acid. The recovery rate of this process is around 85-90 % of the P in the digested sewage sludge through a two-stage process. The first is the digestion of the ash with acid and the second is the removal of impurities (Fe and Al) from the suspension.

The Figure 5.1.14 shows the boundaries of the systems comprising the PARFORCE process. The PARFORCE process recovers the phosphorus contained in the SSA generated during the incineration of the sewage sludge. The residues of the ash used in the PARFORCE process are subsequently landfilled. It was estimated that the 60.56 kg of DM 20% sludge produced during the wastewater treatment process gives approximately 5.45 kg of SSA after incineration (assuming that 45 % of the dry matter in the sludge was mineral and that this mineral matter was totally in the SSA). It has been estimated that the PARFORCE process recovers approximately 1.33 kg of H_3PO_4 at 75 % which is equivalent to 0.54 kg of P_2O_5 in terms of phosphorus. It is therefore necessary to add 0.26 kg of P_2O_5 to obtain the 0.8 kg of P_2O_5 targeted by the functional unit, which is equivalent to 0.54 kg of TSP. The above equivalences are based on a stoichiometric conversion of phosphorus.

It is important to note that the balance made above is based on the amount of P and more precisely P_2O_5. The fact that the PARFORCE process produces 75 % phosphoric acid (H_3PO_4), which is a product with a high added-value, is therefore not valued except for its phosphorus content.

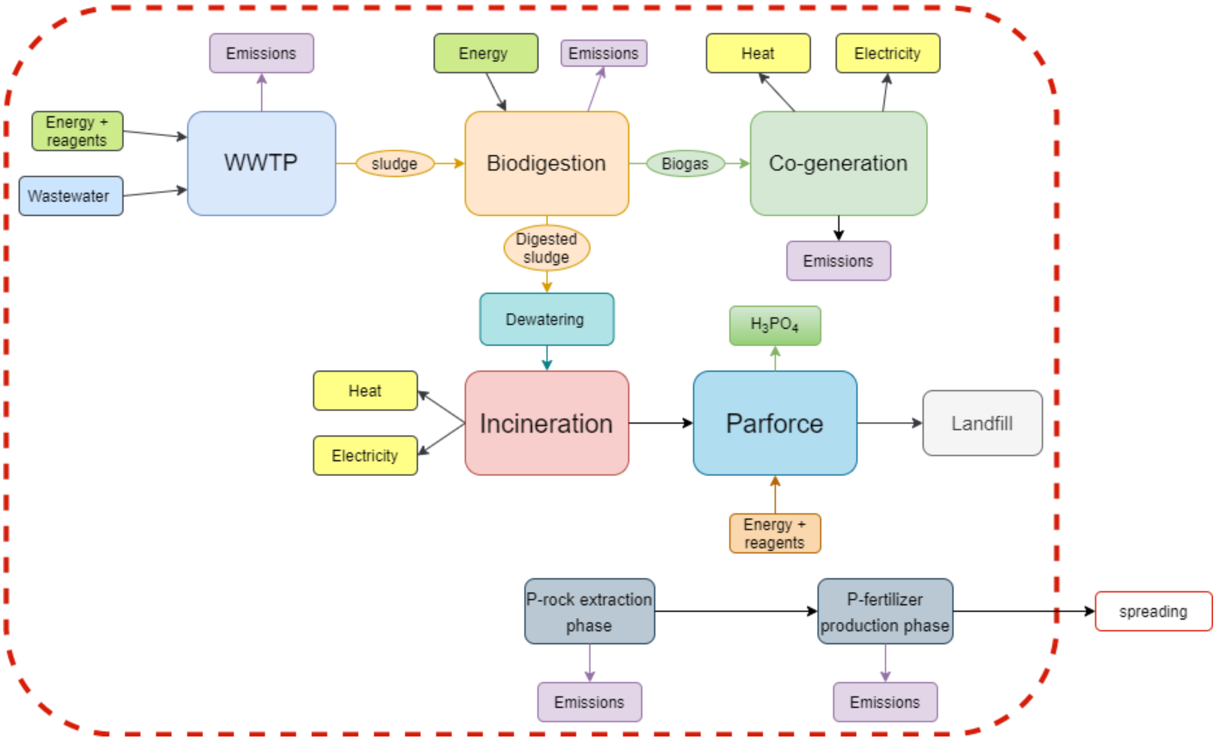


Figure 5.1.14: System boundaries for the PARFORCE process in the multifunctional system

The Figure 5.1.15 shows the impacts of the different part of the PARFORCE system. The impacts of the PARFORCE process (in blue) are mainly on the categories of fossil fuel depletion, climate change and to a minor extent mineral resource depletion. The impact of TSP production (in dark blue) is predominantly on the mineral resource depletion category.

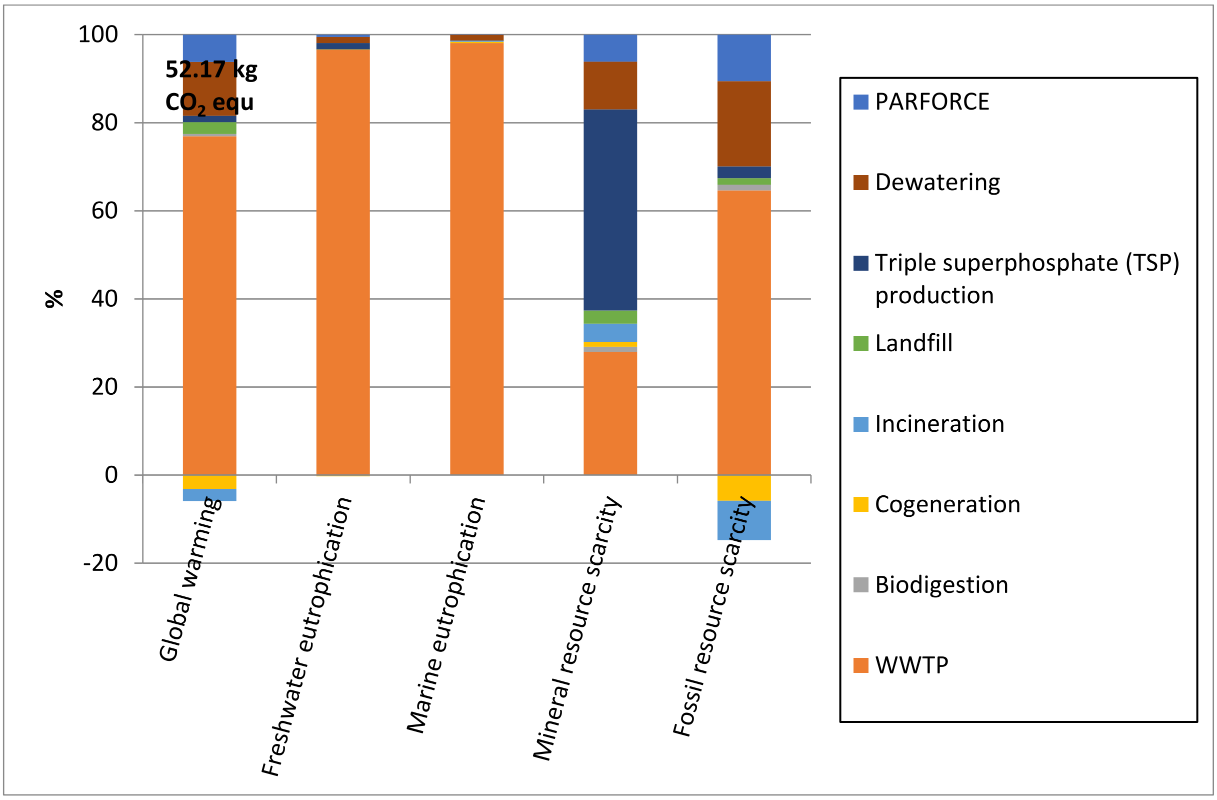


Figure 5.1.15: Environmental impacts of the multifunctional system including 100 m³ of treated water in the WWTP, the P recovery from the sewage sludge in PARFORCE process and the additional production of chemical P to obtain 0.80 kg of P_2O_5– Characterisation ReCiPe 2016 H/World H

The Figure 5.1.16 shows the impacts of producing 1 kg of H_3PO_4 using the PARFORCE process without the landfill of SSA residues. Here only the environmental performance of the PARFORCE process itself is studied, the production of the sewage sludge and the incineration of the latter to produce the SSA used by the process are not taken into account. The use of hydrochloric acid (yellow), electricity (light orange) and heat (dark blue) have the greatest impact on the categories of global warming and depletion of fossil resources. The beneficial environmental effects of avoided sodium chloride production are also visible (in grey) across all categories.

In order to reduce the environmental impacts of the process, it should be verified that the use of hydrochloric acid as well as the consumption of electricity are fully optimised as they cause significant environmental impacts.

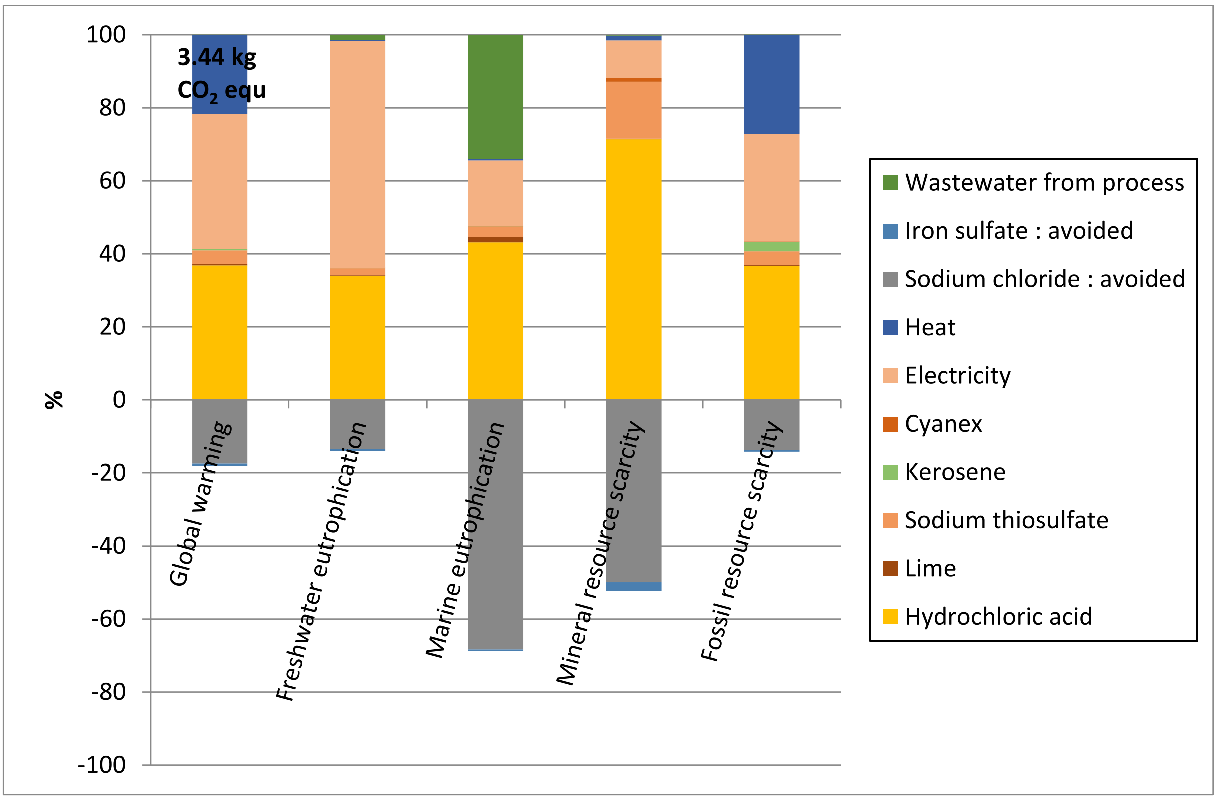


Figure 5.1.16: Environmental impacts of the production of 1 kg of H_3PO_4 by PARFORCE process– Characterisation ReCiPe 2016 H/World H

Given the nature of the final product (phosphoric acid), an additional comparison will be made for the PARFORCE process. Here, the impact of producing 1 kg of H_3PO_4 by the PARFORCE process is compared to the impact of the conventional production process (modelled using the corresponding Ecoinvent entry). Figure 5.1.17 shows the results of this comparison.

The impacts of conventional production are significantly lower for the categories of climate change, freshwater eutrophication and fossil resource scarcity. However, the impact of conventional production on the category of mineral resource depletion is much greater than that of the PARFORCE process.

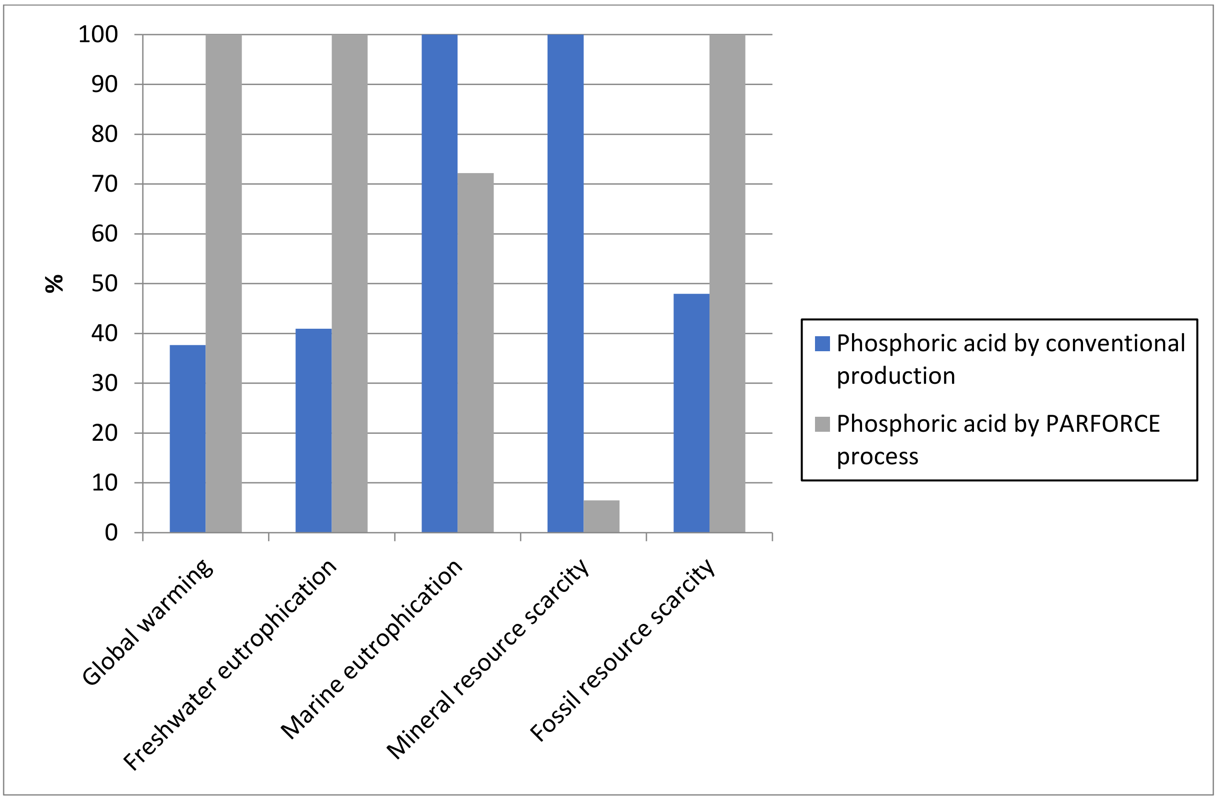


Figure 5.1.17: Comparison of the environmental impacts of producing 1 kg of H_3PO_4 by conventional production and by the PARFORCE process– Characterisation ReCiPe 2016 H/World H

The Figure 5.1.18 shows a comparison of the environmental impacts of the Parforce system and the reference system. The impacts of the PARFORCE system on the categories of global warming and fossil fuel depletion appear to be higher, while the impact on mineral resource depletion is lower for the PARFORCE system. This is due to the landfilling of residues in the PARFORCE process and the impactful steps of the process itself (consumption of hydrochloric acid, electricity and heat). The low impact of the system on the depletion of mineral resources in the PARFORCE system is explained by the good P recovery in the SSA (between 85 and 90 %). Of these differences, only the difference in the mineral resource scarcity category is considered significant as the differences in the climate change and fossil resource scarcity categories do not reach the required 10% (Jolliet et al. 2015).

It is also important to bear in mind that phosphoric acid production is considered just for its P content in this study. The high added value of the product of the PARFORCE process is therefore not fully taken into account.

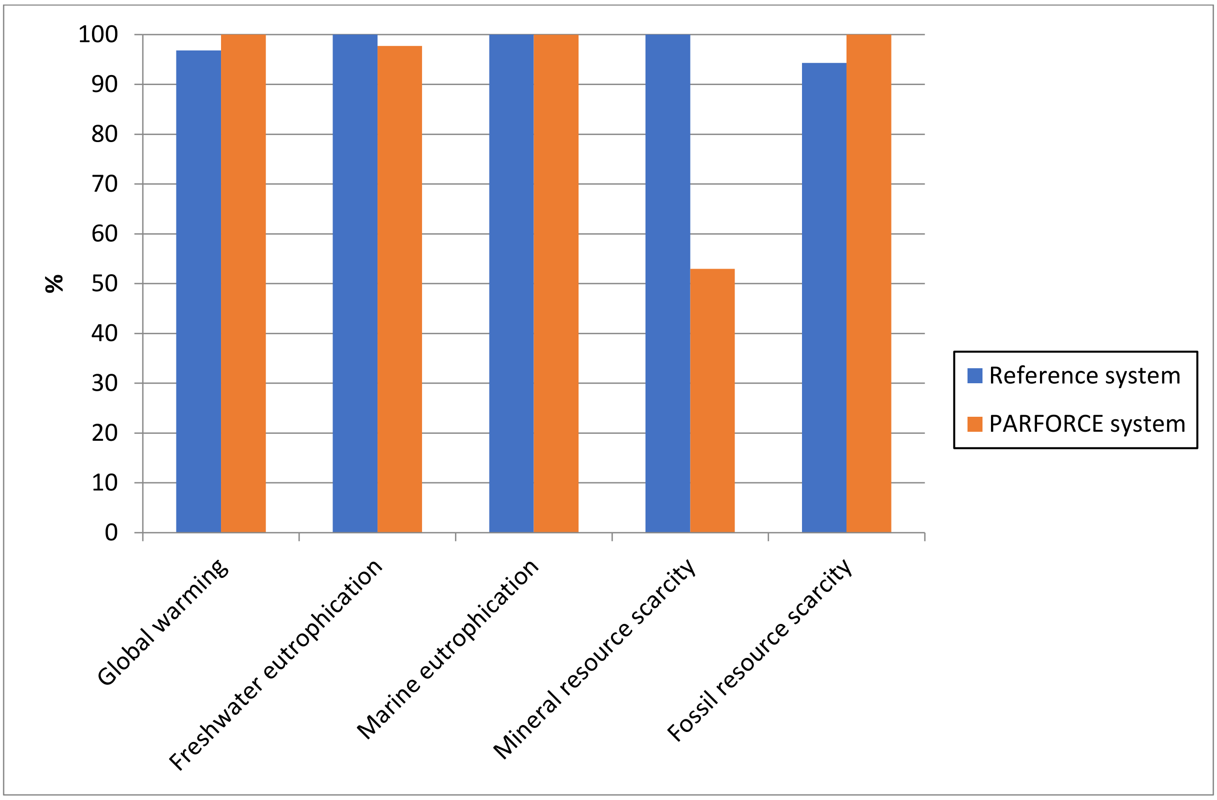


Figure 5.1.18: Comparison of the environmental impacts of the PARFORCE system and the reference system– Characterisation ReCiPe 2016 H/World H

5.1.2.5 *LCA of the PULSE system*

The PULSE process is a chemical extraction process directly from the digested sludge. The key steps include drying and grinding the sludge, acid leaching, solvent extraction of impurities (such as Cd, Cu, Fe, Pb and Zn) and finally precipitation of phosphorus as calcium phosphate by increasing the pH. During the process, the acid is recycled and a 2 % loss per batch is taken into account. The basic solution used for solvent regeneration is also recycled at a rate of 50 %. The details of the process are available in the chapter 3.4 dedicated to the explanation of the implementation of the PULSE process. The final P-material has the advantage of having a rather high P_2O_5 concentration of about 27%.

Figure 5.1.19 shows the boundaries of the system including the PULSE process. The PULSE process takes place after sludge dewatering. After dewatering the sludge to about DM 20 %, the sludge is dried to about DM 95 % in an industrial dryer (natural gas powered). The choice to use the consumption of an industrial dryer was made in order not to bias the results with the consumption of the pilot scale dryer used here. The residual sewage sludge after the process is incinerated with recovery of electricity and heat. The used solids are also treated by incineration. The incineration residues are in both cases landfilled.

It was estimated that the PULSE process produced 0.72 kg P_2O_5 equivalent from the 60.57 kg DM 20% of sludge produced when treating 100 m³ of wastewater. It therefore remains to produce 0.08 kg of P_2O_5 by chemical means to reach the 0.8 kg of P_2O_5 of the functional unit, which is equivalent to a chemical production of 0.17 kg of TSP at 48% P_2O_5.

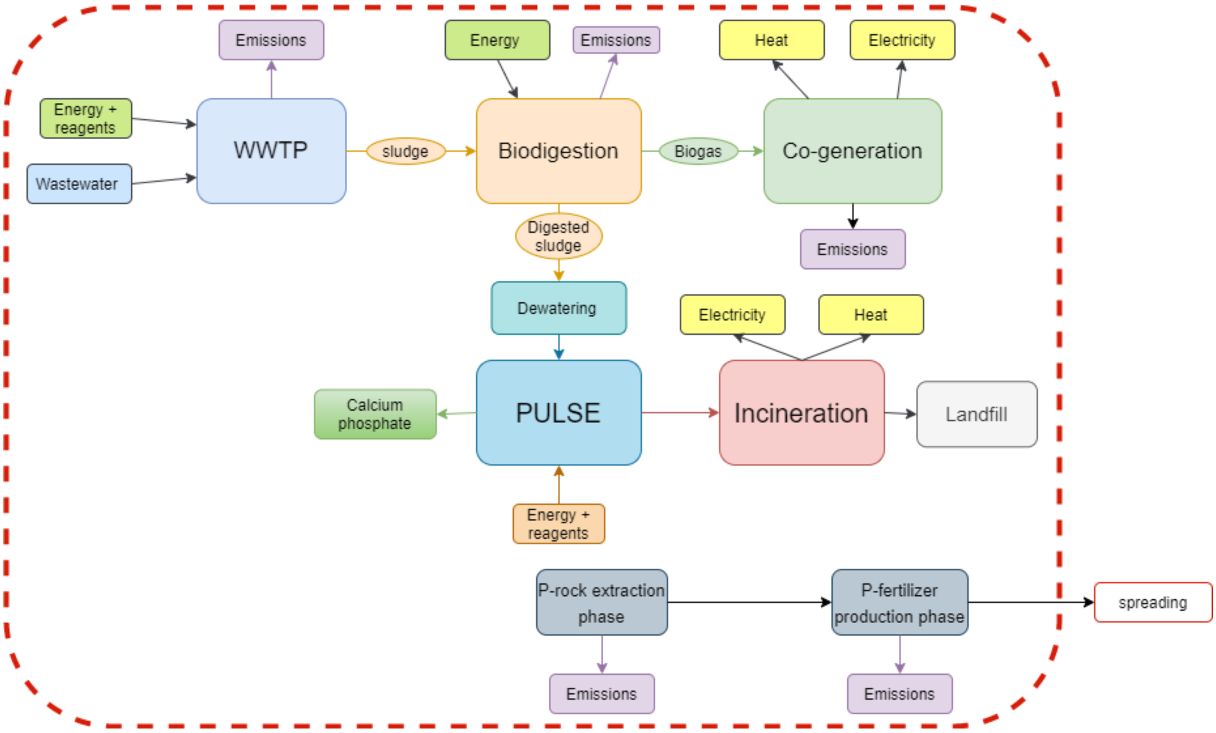


Figure 5.1.19: System boundaries for the PULSE process in the multifunctional system

Figure 5.1.20 shows the environmental impacts of the system including the PULSE process. It can be seen that the process itself (in blue) is responsible for the major part of the impacts in the categories of global warming, fossil and mineral resource depletion. In addition to the remarks common to all systems, it is also important to note the impact of landfill (in green) which is not negligible on the categories of mineral and fossil resource depletion and global warming.

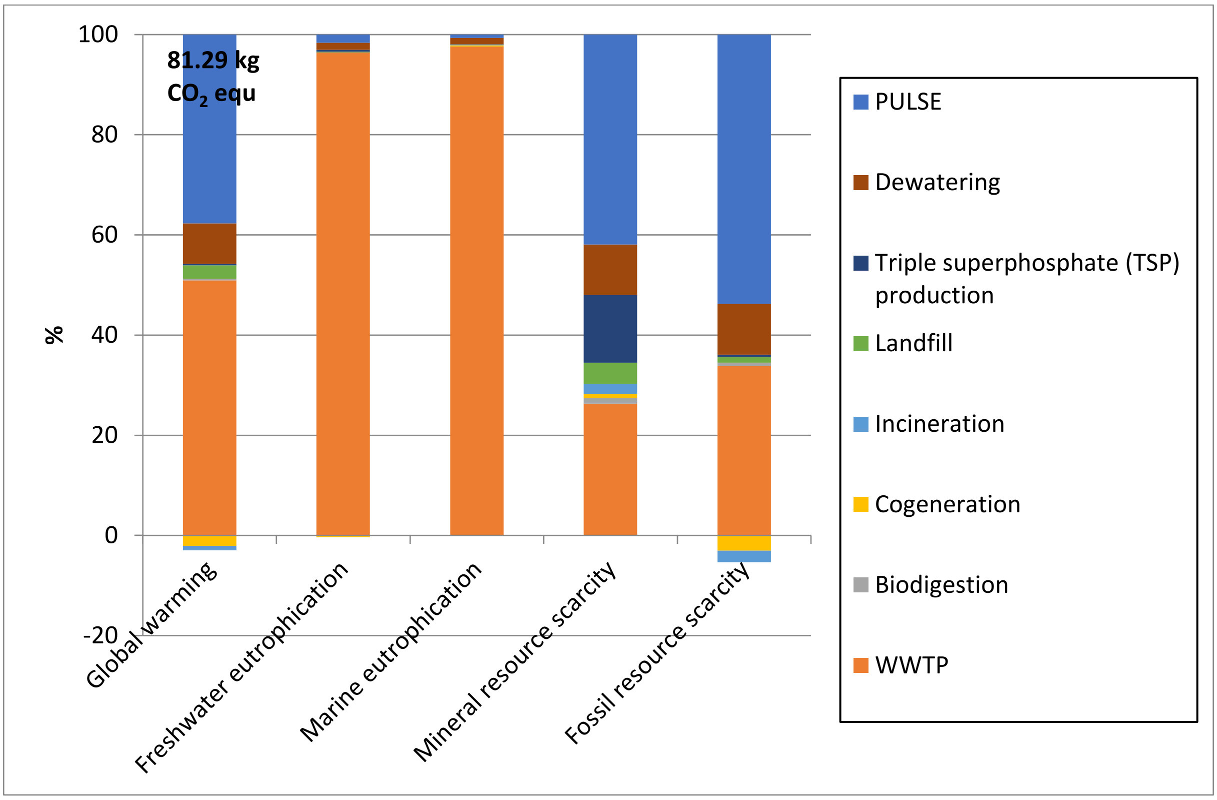


Figure 5.1.20: Environmental impacts of the multifunctional system including 100 m³ of treated water in the WWTP, the P recovery from the sewage sludge in PULSE process and the additional production of chemical P to obtain 0.80 kg of P_2O_5– Characterisation ReCiPe 2016 H/World H

Figure 5.1.21 shows the environmental impacts of producing 1 kg of P_2O_5 by the PULSE process. Only the treatment of sewage sludge free of environmental loads for the production of 1 kg P_2O_5 is considered here. Waste treatment (in dark orange) is responsible for significant impact on global warming and marine eutrophication. This is due to the incineration of residual sewage sludge and the incineration of spent solvent. The extraction phase (in light orange) is responsible for the most of impacts on all categories. This is principally due to the use of a basic solution used to regenerate the extraction solvent. The drying phase (in yellow) is also responsible for significant impacts, which is logical given the use of natural gas.

One way of reducing these impacts would be to use a solar dryer in order to reduce the environmental impact of the drying step. Another possibility to reduce the impacts of drying would be to integrate the PULSE process energetically by recovering part of the thermal energy from the incinerator to dry the sludge. It would also be interesting to optimise the recycling of the base used for the regeneration of the solvent.

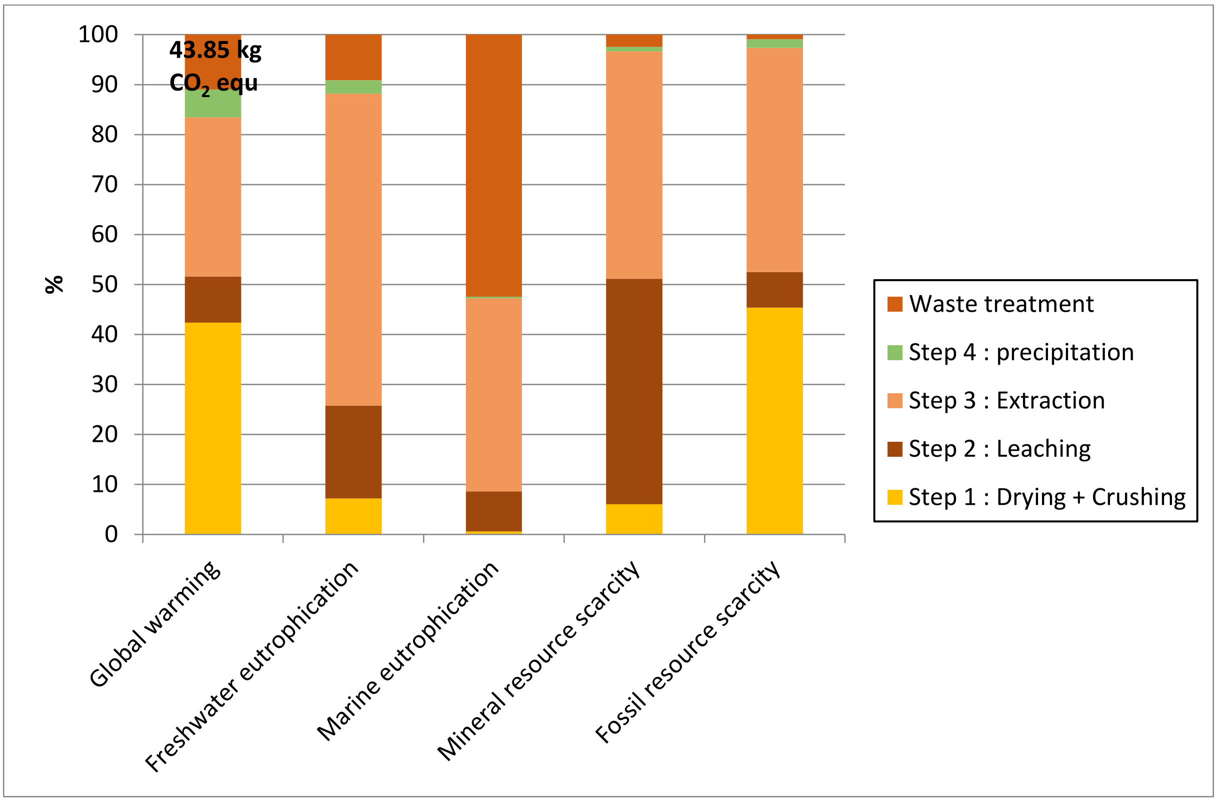


Figure 5.1.21: Environmental impacts of the production of 1 kg of P_2O_5 by PULSE process– Characterisation ReCiPe 2016 H/World H

Figure 5.1.22 shows the comparison of the environmental impacts of the PULSE system and the reference system. The impacts of the PULSE system appear to be greater for all categories studied except for the mineral resource scarcity where the recuperation of P-material has a beneficial impact.

The observed differences are significant for the climate change categories, mineral and fossil resource scarcity.

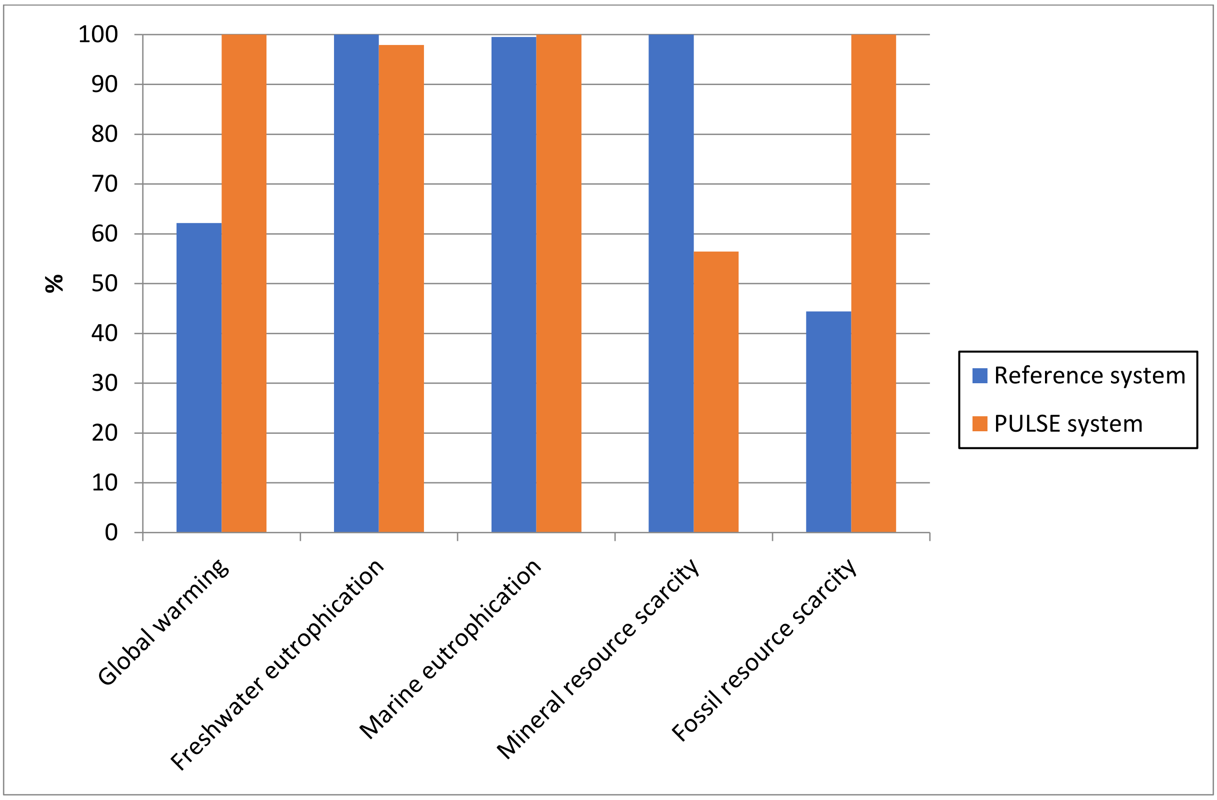


Figure 5.1.22: Comparison of the environmental impacts of the PULSE system and the reference system– Characterisation ReCiPe 2016 H/World H

It is important to note that the electrical consumption of pumps and agitators are based on the consumption of the pilot demonstrator. These consumptions can therefore be reduced by considering technical equipment of industrial scale.

A second optimisation potential is that the environmental impacts of the solvent extraction step in the PULSE process can be further reduced by decreasing the base consumption during solvent regeneration. An alternative would be to use an electrochemical process to implement the pH shifts for the solvent regeneration step.

5.1.3 Discussion of results for LCA with system expansion approach

The most impacting steps have been identified for each system:

- for the EuPhoRe® process: electricity, chemicals and natural gas (for the starting procedure) and large benefits from heat recovery
- for the Struvia™ process: electricity and flocculant (polymer).
- for the Parforce process: use of hydrochloric acid, electricity and heat
- for PULSE process: waste treatment, organic solvent and electricity

In conclusion, the environmental performance study with the perspective of system expansion showed that P recovery as realised in the EuPhoRe® and Struvia™ demonstrators presents environmental advantages over the conventional chemical route to produce P fertiliser.

The PULSE and PARFORCE processes appear to have higher environmental impacts than the reference system. However, it is important to note that these processes produce P-material that can have a high added value (70% phosphoric acid and 27% calcium phosphate P_2O_5). The major advantage of all the processes studied is that they allow the relocation of phosphorus fertiliser and to more independence for the EU regarding P importation from other continents.

This conclusion is different of the one from(Pradel and Aissani 2019)(Pradel and Aissani 2019)(Pradel and Aissani 2019)(Pradel and Aissani 2019)(Pradel and Aissani 2019) Pradel and Aissani 2019). Indeed, they concluded that phosphorus recovery processes from sewage sludge were less environmentally friendly than conventional production by basing their LCA on the calculation of an allocation factor distributing the environmental impacts of the sewage treatment plant between the wastewater treatment and sludge production functions. This allocation factor was based on physical parameters of the wastewater treatment line. These differing conclusions are therefore not surprising given that the means of accounting for the wastewater treatment plant is drastically different from one study to another. Furthermore, these differences highlight the importance of taking into account several methodological approaches in order to confirm the conclusions in the environmental assessment of sewage sludge-based nutrient recovery processes.

In order to confirm the results and make the conclusions more robust, another LCA approach was considered. The avoided burden method will now be developed for application to the systems studied.

5.2 Avoided burden methodology

5.2.1 Methodological choices

The avoided burden method is an LCA methodology that allows the co-products of a system to be taken into account without extending the boundaries of the system (as the system expansion method does) and without the use of allocation factors (which are difficult to implement and often disputed).

This method consists of taking into account the co-product by subtracting the environmental impacts of the production that this co-product replaces from those of the system as a whole. The avoided burden approach applied to this project consists of studying the environmental impacts of a system including the treatment of a quantity of wastewater and the treatment of the sewage sludge through the introduction of a phosphorus recovery process. The environmental impacts of the phosphorus fertiliser production are also studied in order to subtract the environmental impacts of the avoided mineral fertiliser production through the recovery process from the total impacts of the system studied. Following this approach, the functional unit of the systems studied is the treatment of 100 m^3 of wastewater and the corresponding treatment of sewage sludge. The phosphorus-rich products of the different recovery processes are taken into account as avoided mineral fertilisers. In the modelling of these mineral fertilisers, it is the production of triple super phosphate (TSP) that is considered.

The data used for the environmental assessment of the WWTP correspond to the WWTP of Liège-Oupeye (438,000 PE, Wallonia, Belgium) and are provided by the AIDE. This plant is chosen because it is representative of large and relatively modern (2007) Belgian WWTP. A biodigestion unit is added to be closer to what is done in most of the European WWTP (especially German or French). The electricity consumptions were modelled with the German mix of 2016 using the corresponding Ecoinvent entry. A sensitivity analysis was performed by comparing the impacts of the modelled systems with the German (2016), French (2016) and Belgian (2016) mix, this analysis will be detailed below.

The data for direct emissions are calculated on the basis of the relevant scientific literature and the inputs and outputs of the WWTP are modelled using generic data from the Ecoinvent database.

The Ecoinvent database was also used to model biodigestion of sludge, cogeneration of biogas, dewatering and incineration of digested sludge with energy recovery and landfill operations.

The data for the recovery processes was received directly from the partners and the modelling of the inputs and outputs was generally done using the Ecoinvent database.

Finally, a sensitivity analysis was also carried out on the phosphorus content of the sewage sludge used with the avoided burden method. Indeed, it is common for the P content of sewage sludge to vary according to regional and climatic factors and the origin of the treated wastewater. To study the reaction of each phosphorus recovery process to these variations, a sensitivity analysis was carried out on this factor. The influence of these variations was discussed with the owners of the technologies in order to best model these changes in an appropriated way for each demonstrator.

5.2.2 Results for four recovery processes

5.2.2.1 *LCA of the reference system*

Introduction

The reference case for the avoided burden method is very similar to that of the expansion system method with the difference that the fertiliser production by the demonstrators is taken into account as avoided TSP production. The impacts of this avoided chemical production are therefore subtracted from the impacts of the studied system.

Figure 5.2.1illustrates the system boundaries of the reference case.

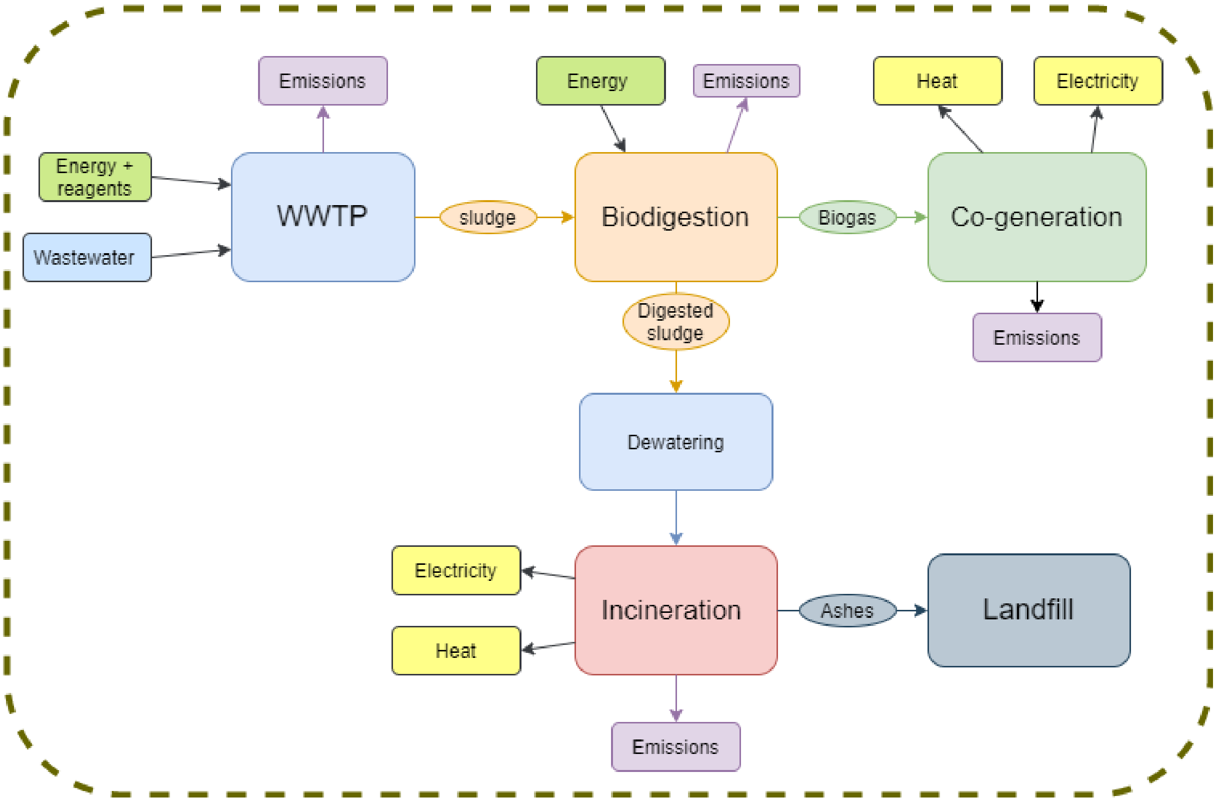


Figure 5.2.1: System boundaries for the reference case with the avoided burden approach

Results of reference system

The results of the reference case are presented in Figure 5.2.2. As shown in the graph, the majority of the environmental impacts are due to the WWTP itself (orange). Logically, biodigestion (grey) is responsible for relatively low environmental impacts (grey) and cogeneration (yellow) and incineration (blue) are responsible for beneficial environmental impacts due to avoided heat and electricity production. The dewatering of the sewage sludge (in brown) has a significant impact on the categories of fossil and mineral resource depletion and global warming, due to the relatively high use of electricity during the dewatering phase and the fact that the electricity used has been modelled on the German electricity mix, which is rich in carbon.

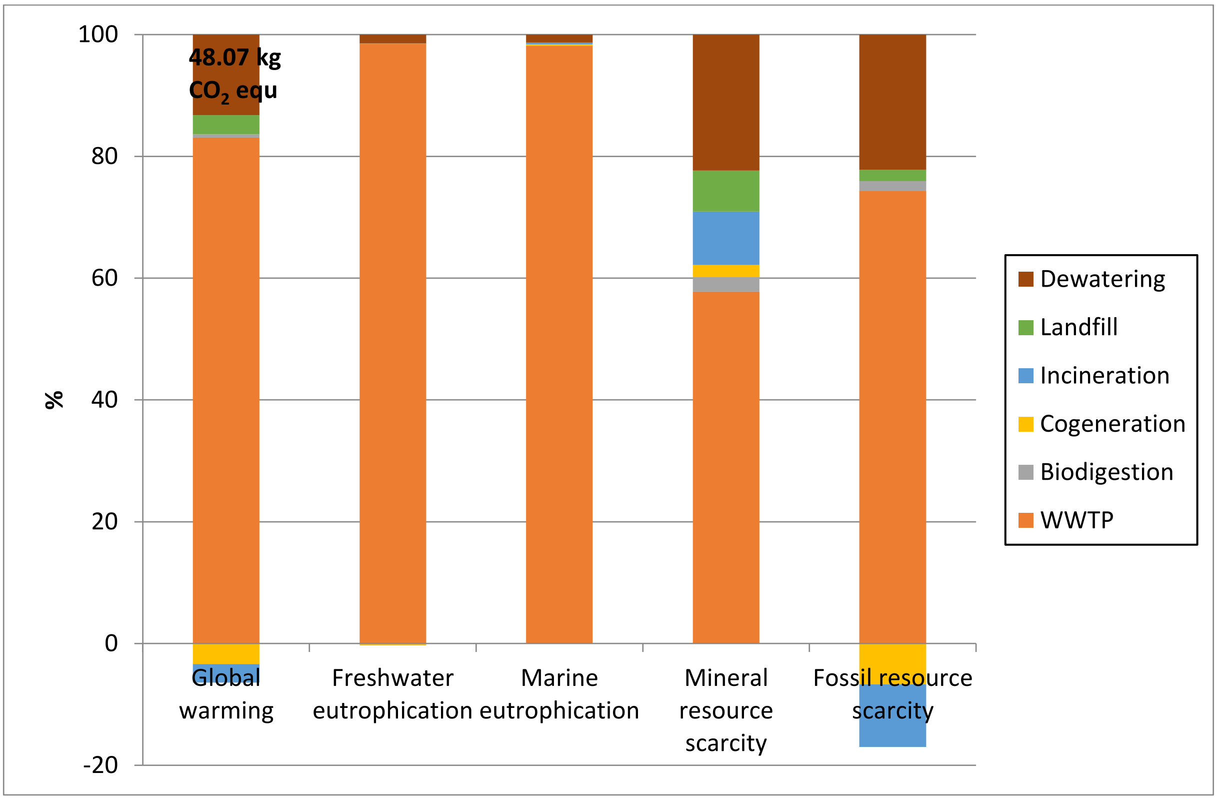


Figure 5.2.2: Environmental impacts of the reference case with the avoided burden approach– Characterisation ReCiPe 2016 H/World H

5.2.2.2 *LCA of the EuPhoRe® recovery system*

Introduction

The system containing the EuPhoRe® recovery process includes the sewage treatment plant, the biodigestion of the sludge from the plant, the cogeneration of the biogas produced during the biodigestion stage, the dewatering of digested sludge before the solar drying, and the treatment of the digested sludge by the EuPhoRe® process with the production of P-rich SSA with bioavailable phosphorus directly usable into fertilising products. Taking into account the amount of sludge resulting from the treatment of 100 m³ of wastewater and the reduction of the sludge volume after biodigestion, the EuPhoRe® process produces 0.79 kg of P_2O_5 from the 60.57 kg of sludge at DM 20 % from the treatment of 100 m³ of wastewater. This P_2O_5 production is taken into account by avoiding the production of 1.64 kg of TSP. The previous equivalence is based solely on the phosphorus content of the products.

Figure 5.2.3 illustrates the system boundaries of the EuPhoRe® case.

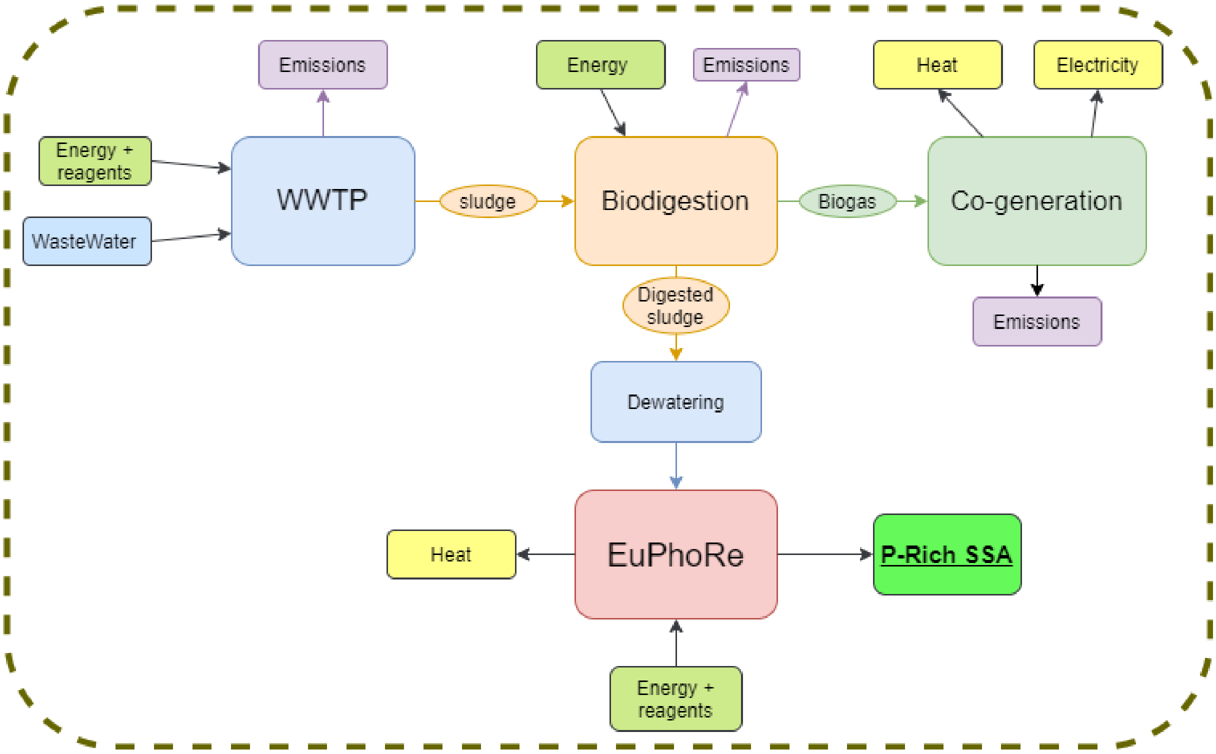


Figure 5.2.3: System boundaries for the EuPhoRe® system with the avoided burden approach

Results of EuPhoRe® system

The results displayed at Figure 5.27 show the beneficial impacts of the EuPhoRe® process itself (in blue) on the categories of global warming and fossil resource depletion. It is also important to note the minor effects of the avoidance of mineral fertilizer production on the various impact categories except for the category of mineral resource depletion where this avoidance has a significant impact (in dark blue). The beneficial effects of cogeneration (in yellow) can be seen mainly in the categories of depletion of fossil resources and global warming. The majority of the environmental effects are still attributable to the WWTP (orange) and dewatering (brown).

Figure 5.2.4 presents the results of the EuPhoRe® case.

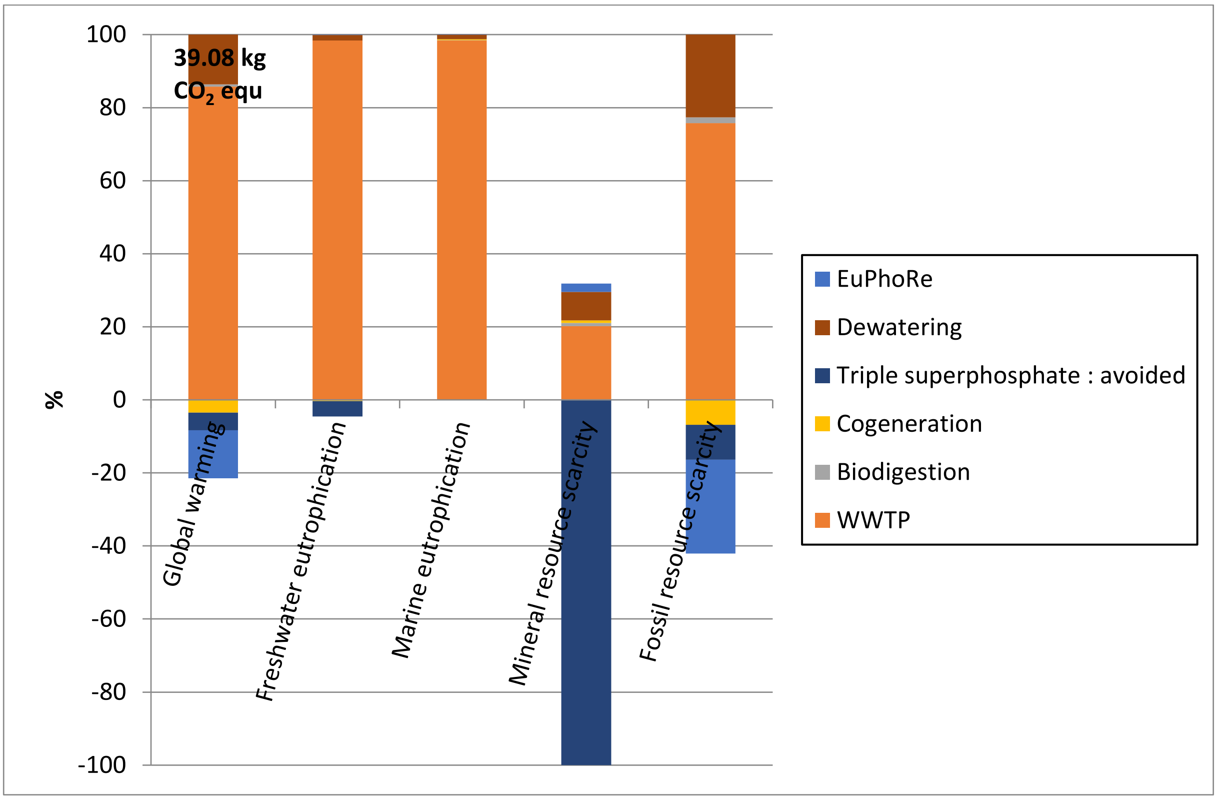


Figure 5.2.4: Environmental impacts of the EuPhoRe® system with the avoided burden approach– Characterisation ReCiPe 2016 H/World H

Figure 5.2.5 compares the environmental impacts of the EuPhoRe® and reference systems with the avoided burden method. The impacts of the EuPhoRe® system appear to be lower for all categories studied. However, the difference for the eutrophication categories does not reach the significance limit (30% for these categories). These results confirm those obtained with the system expansion approach.

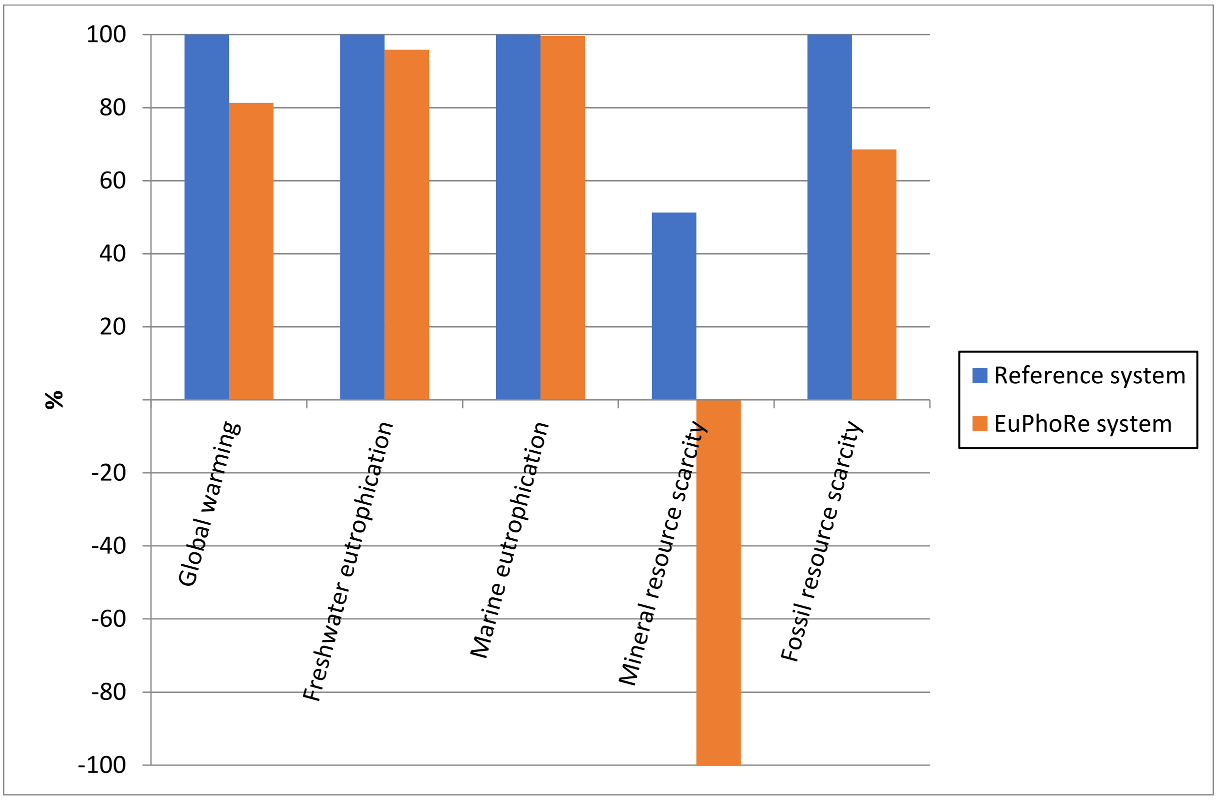


Figure 5.2.5: Comparison of the environmental impacts of the EuPhoRe® system and the reference system with the avoided burden method – Characterisation ReCiPe 2016 H/World H

A sensitivity analysis of the electrical power used will now be carried out. Three electricity mixes will be studied, the first is the German electricity mix of 2016, the second is the Belgian mix of 2016 and the third is the French mix of 2016.

Figure 5.2.6 and Table 5.2.1 below shows the results of the comparison of the system impacts for each of the electricity mixes. The results show that the impacts of the system taking into account the German electricity mix are higher, which is logical given that it is the electricity mix that relies most on fossil fuels. The French mix is more based on nuclear energy which has less impact on the categories of global warming and fossil fuel depletion (radioactivity impacts are not considered). The Belgian mix can be considered as intermediate, as the results show. The impacts on the mineral depletion category are however lower for the German model, which can be explained by a low use of nuclear power, i.e. a lower depletion of the uranium resource.

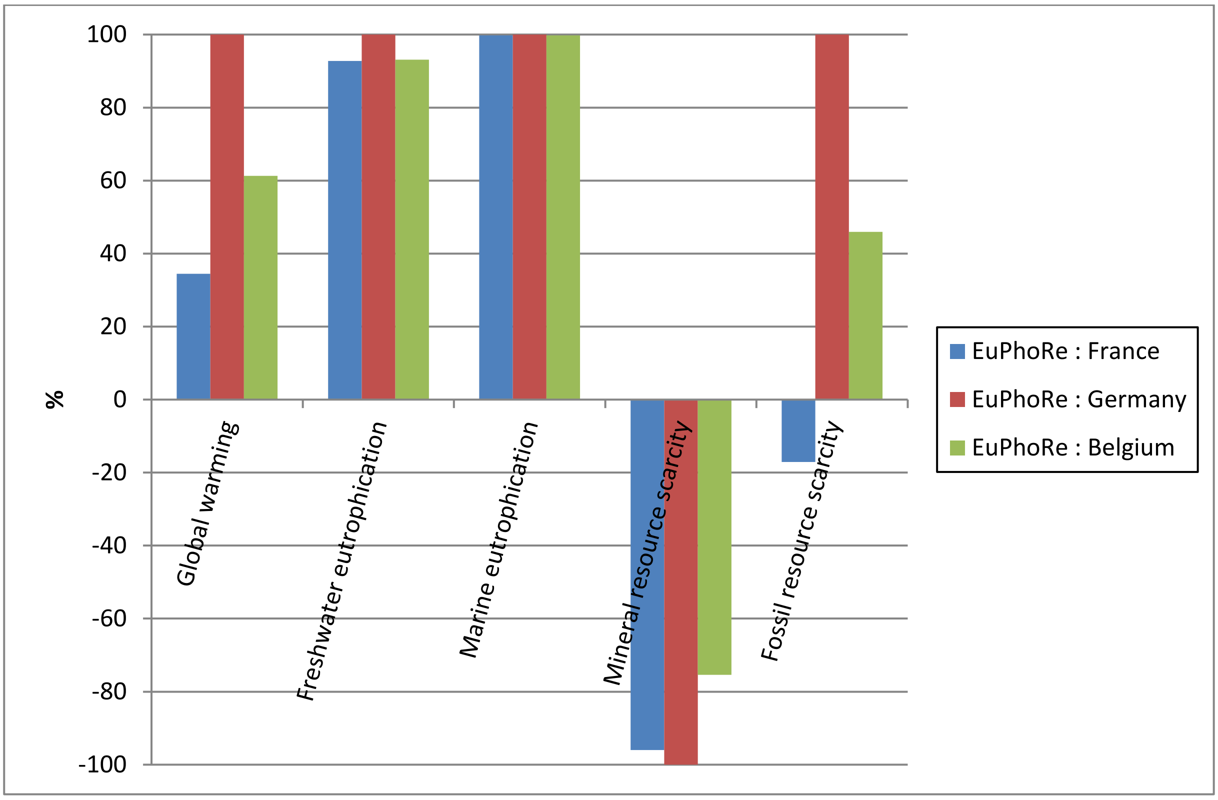


Figure 5.2.6: Comparison of the environmental impacts of the EuPhoRe® system for the three electricity mixes studied (German, Belgian and French) – Characterisation ReCiPe 2016 H/World H

Table 5.2.1: Sensitivity analysis of the environmental impacts of the EuPhoRe® system for the three electricity mixes studied (German, Belgian and French)

Impact category	Unit	EuPhoRe®: France	EuPhoRe®: Germany	EuPhoRe®: Belgium	**Difference: Germany - Belgium**	**Difference : Germany - France**
Global warming	kg CO_2 eq	13.5	39.1	24.0	**-38.7 %**	**-65.6 %**
Freshwater eutrophication	kg P eq	0.0552	0.0596	0.0555	**-6.8 %**	**-7.3 %**
Marine eutrophication	kg N eq	0.0927	0.0929	0.0927	**-0.2 %**	**-0.2 %**
Mineral resource scarcity	kg Cu eq	-0.1384	-0.1441	-0.1086	**24.6 %**	**4.0 %**
Fossil resource scarcity	kg oil eq	-0.9	5.2	2.4	**-54.0 %**	**-117.0 %**

A sensitivity analysis on the P_2O_5 content of the sludge was also carried out on the EuPhoRe® process. In the modelling of this sensitivity analysis, the Belgian electricity mix of 2019 was used, mainly because it can be considered as intermediate between the German and French electricity mix. It was discussed with the process holder that a variation in the sludge content used only affects the P_2O_5 content of the recovered SSA given the nature of this thermo-chemical process and the almost complete recovery of phosphorus from the sludge. The sensitivity analysis considers a variation of plus and minus 30 % in the P_2O_5 content of the sludge used, which translates into a variation of plus and minus 30 % in the P_2O_5 content of the recovered SSA. The P_2O_5 content of SSA is 16 % in the normal case, which drops to 11.2 % in the case of a minus 30 % change and rises to 20.8 % in the case of a plus 30 % increase. The process consumptions have been updated taking into account these changes in P_2O_5 content in the SSA. These variations also have the effect of increasing or decreasing the amount of P_2O_5 recovered from the 60.57 kg of sludge at DM 20 % from the treatment of 100 m^3 of wastewater. In the case of a variation of plus 30 %, the quantity of recovered P_2O_5 increases from 0.79 kg to 1.01 and this quantity decreases to 0.55 kg for a 30 % decrease in the P content of the sludge. Figure 5.2.7 and Table 5.2.2 show the results of the sensitivity analysis on phosphorus content.

In general, the impacts increase when the phosphorus content decreases for the categories of fossil fuel depletion and global warming, but also and especially for mineral resource depletion.

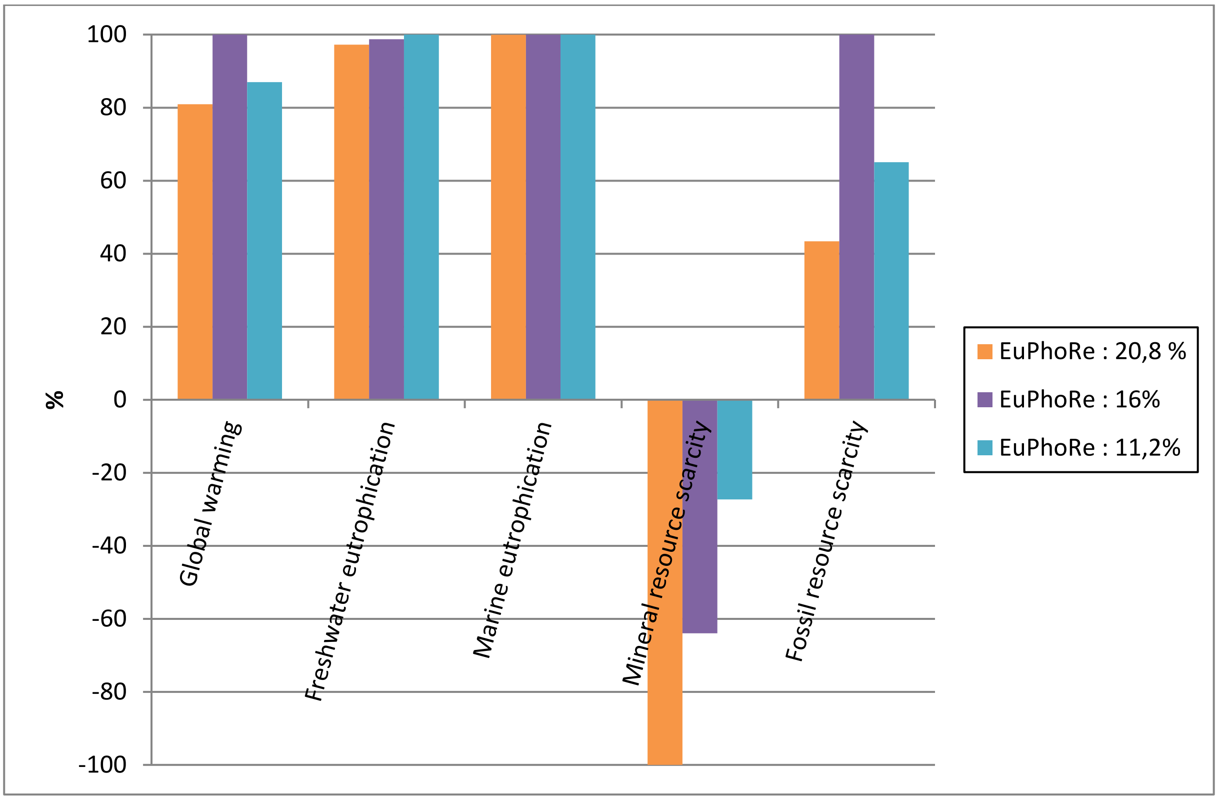


Figure 5.2.7: Comparison of the environmental impacts of the EuPhoRe® system for the three levels of P_2O_5 content of the SSA studied (16 %: reference, 11.2 %: down and 20.8 %: up)– Characterisation ReCiPe 2016 H/World H

Table 5.2.2: Sensitivity analysis of the environmental impacts of the EuPhoRe® system for the three levels of P_2O_5 content studied (16%: reference, 11.2%: down and 20.8%: up)

Impact category	Unit	EuPhoRe® $[P_2O_5]_{SSA}$= 20,8 %	EuPhoRe® $[P_2O_5]_{SSA}$= 11,2 %	EuPhoRe® $[P_2O_5]_{SSA}$= 16 %	**Difference: reference - down**	**Difference: reference - up**
Global warming	kg CO_2 eq	19.4	20.9	24.0	**-13.0 %**	**-19.0 %**
Freshwater eutrophication	kg P eq	0.05465	0.05619	0.05549	**1.3 %**	**-1.5 %**
Marine eutrophication	kg N eq	0.09271	0.09275	0.09273	**0.019 %**	**-0.021 %**
Mineral resource scarcity	kg Cu eq	-0.170	-0.046	-0.109	**57.3 %**	**-56.4 %**
Fossil resource scarcity	kg oil eq	1.0	1.6	2.4	**-34.9 %**	**-56.7 %**

5.2.2.3 *LCA of the PARFORCE recovery system*

Introduction

The principle of the PARFORCE process is to treat the sludge from the incineration of sewage sludge through the addition of additives (especially acid) allowing the recovery of H_3PO_4, road salt (NaCl) and $FeSO_4$ in solution.

This system includes the wastewater treatment plant, sludge biodigestion, biogas cogeneration, dewatering of digested sludge and finally the incineration with recovery of part of the energy in the form of heat and electricity, and then the PARFORCE recovery process for the production of phosphorus products from the SSA. Taking into account the quantity of sludge produced by the treatment of 100 m³ of wastewater (60.57 kg at DM 20%), the quantity of sludge digested and then the quantity of SSA recovered after incineration of this sludge was estimated at 5.45 kg of SSA. From this amount of SSA, the PARFORCE recovery process extracts around 1.33 kg of H_3PO_4 at 75 %. This production is taken into account as an avoided product, as explained before.

Figure 5.2.8 illustrates the system boundaries of the PARFORCE case.

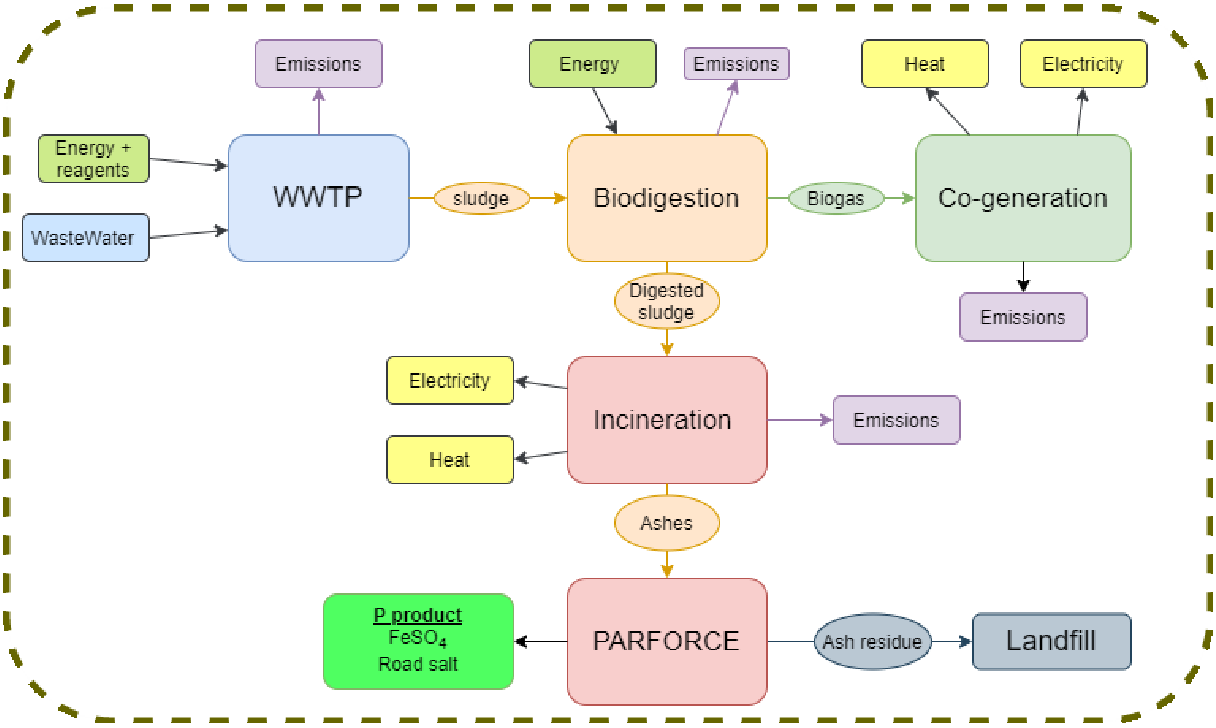


Figure 5.2.8: System boundaries for the PARFORCE system with the avoided burden approach

Results of PARFORCE system

Figure 5.2.9 presents the results of the PARFORCE system. The results of the impact assessment of the PARFORCE system show the minor deleterious impact on the global warming category and the use of fossil and mineral resources of the PARFORCE process (in blue). The beneficial effect in dark blue is due to the avoided production of phosphoric acid as well as cogeneration (yellow) and incineration (light blue). The positive effect of avoiding phosphoric acid production (in blue) is visible mainly in the category of mineral resource depletion and to a minor extent in the categories of fossil resource depletion and global warming. The dewatering phase (brown) has significant impacts on global warming categories and depletion of mineral and fossil resources.

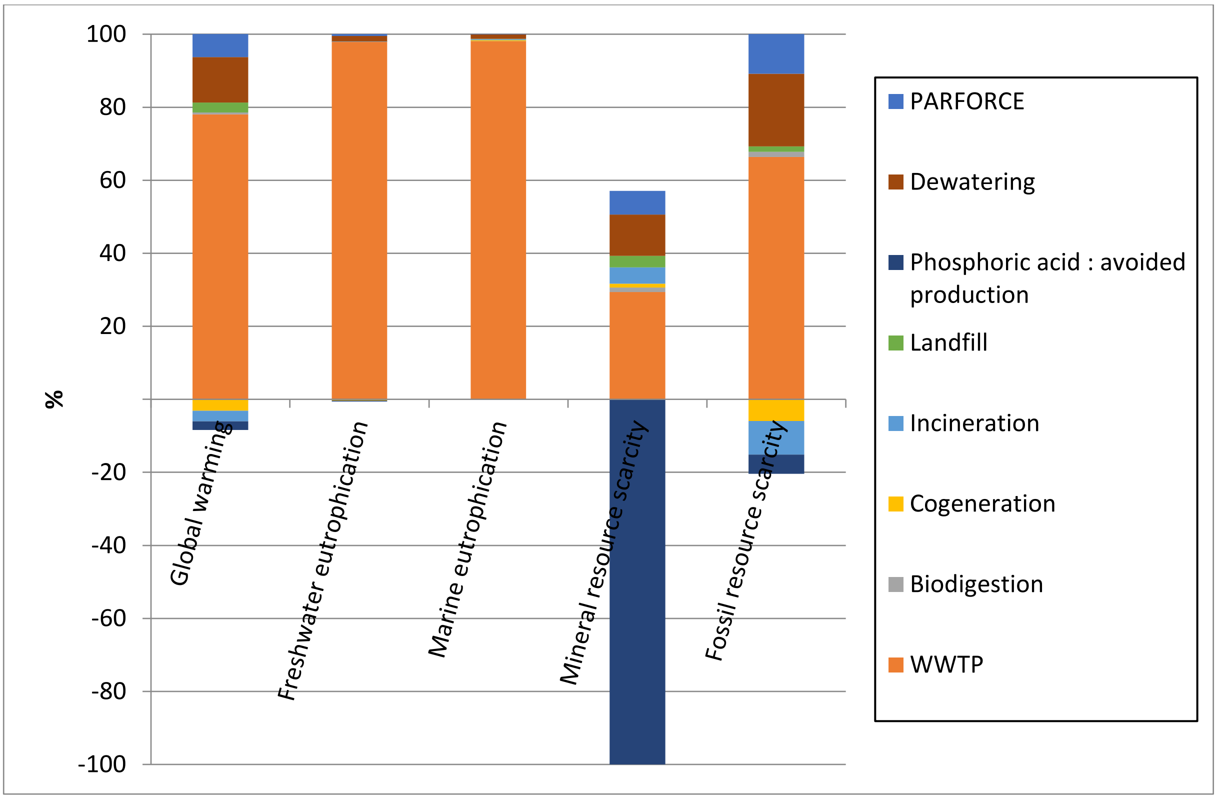


Figure 5.2.9: Environmental impacts of the PARFORCE system with the avoided burden approach– Characterisation ReCiPe 2016 H/World H

Figure 5.2.10 shows the comparison of the environmental impacts of the PARFORCE system and the reference system for the avoided burden method. The impacts of the PARFORCE system appear to be slightly greater for the categories of global warming and fossil fuel depletion. However, the system seems to have much less impact on the category of mineral resource depletion. Similar to the assessment carried out with the system expansion approach, the only significant difference is that there is a difference in the category of mineral resource scarcity, which confirms the previous results.

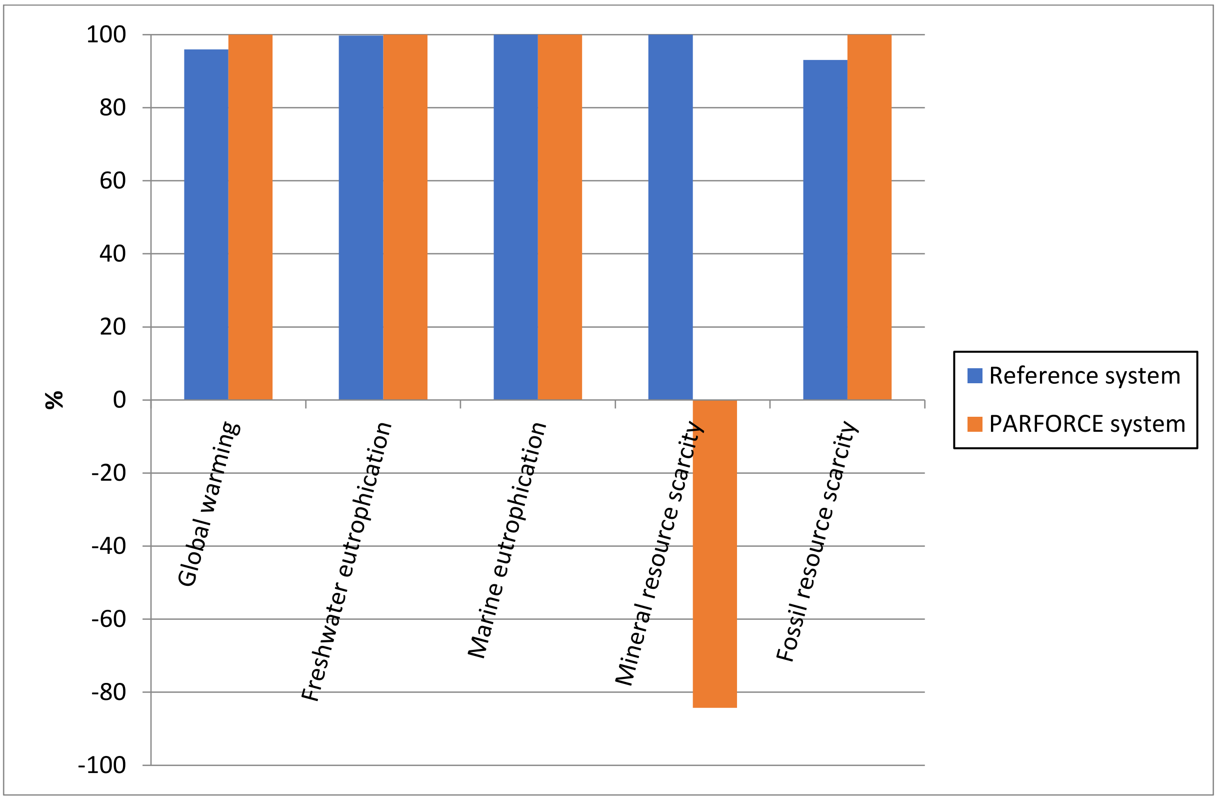


Figure 5.2.10: Comparison of the environmental impacts of the PARFORCE system and the reference system with the avoided burden method – Characterisation ReCiPe 2016 H/World H

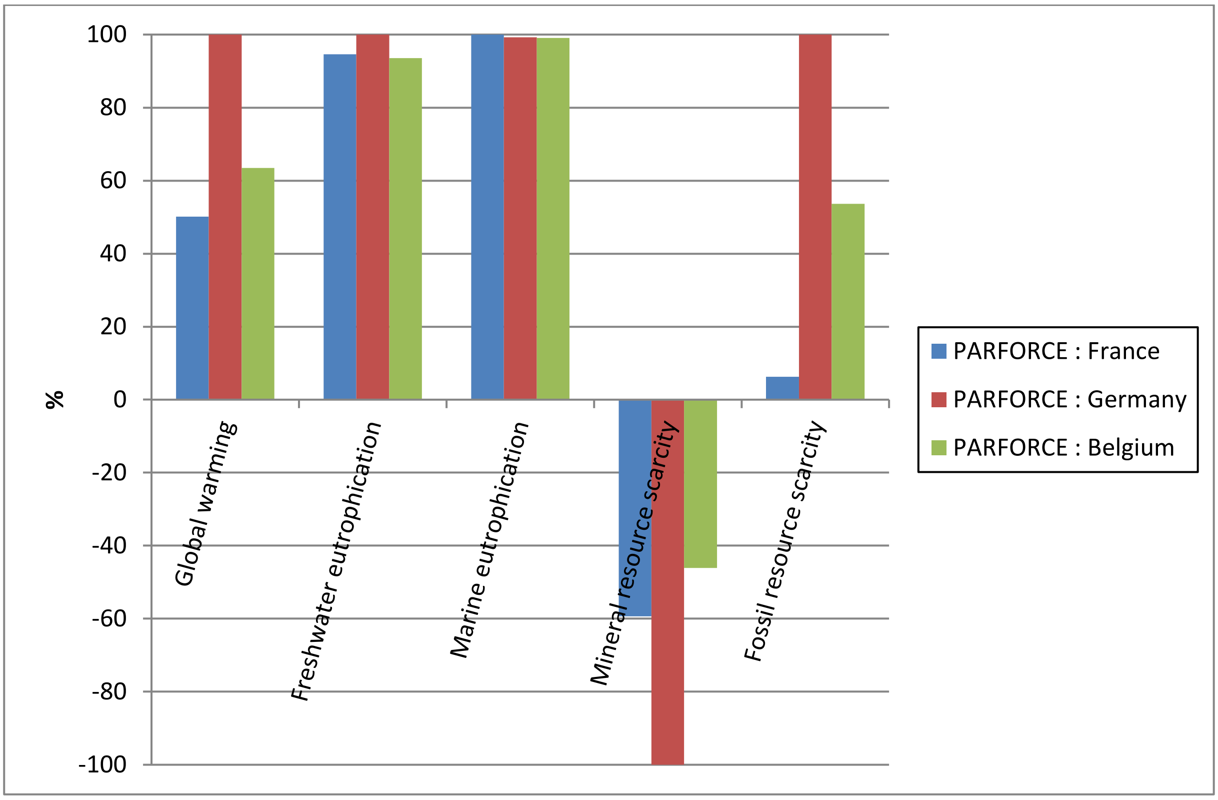


Figure 5.2.11 and Table 5.2.3 shows the results of the sensitivity analysis carried out on the origin of the electricity mix used when modelling the PARFORCE system. The observed differences can be explained by the different electricity mix, the German mix relies more on fossil fuels which impacts more on the categories of global warming and depletion of fossil fuels whereas the French mix relies more on nuclear energy (radioactivity impacts are not considered). The Belgian mix can be considered as intermediate.

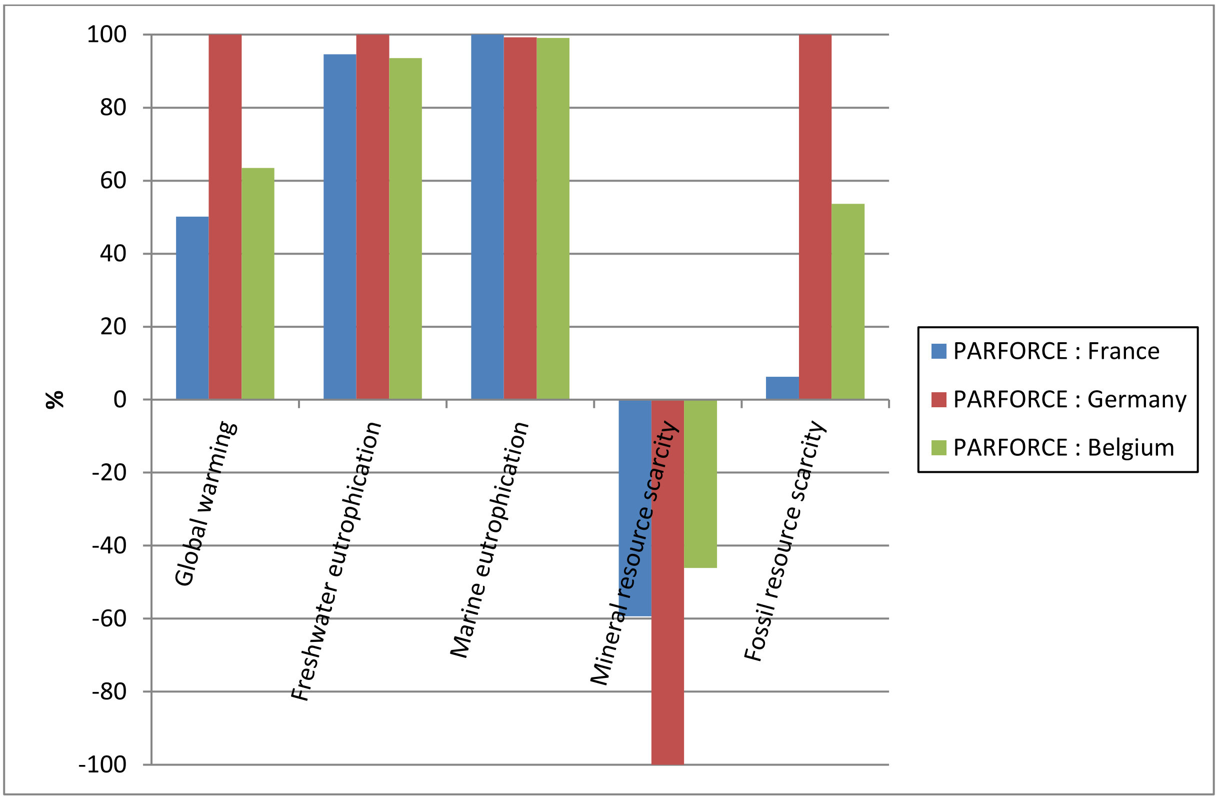


Figure 5.2.11: Comparison of the environmental impacts of the PARFORCE system for the three electricity mixes studied (German, Belgian and French) – Characterisation ReCiPe 2016 H/World H

Table 5.2.3: Sensitivity analysis of the environmental impacts of the PARFORCE system for the three electricity mixes studied (German, Belgian and French)

Impact category	Unit	PARFORCE: France	PARFORCE: Germany	PARFORCE: Belgium	**Difference: Germany - Belgium**	**Difference: Germany - France**
Global warming	kg CO_2 eq	25.1	50.1	31.8	**-36.5 %**	**-49.9 %**
Freshwater eutrophication	kg P eq	0.0590	0.0623	0.0583	**-6.4 %**	**-5.4 %**
Marine eutrophication	kg N eq	0.0940	0.0932	0.0931	**-0.2 %**	**0.8 %**
Mineral resource scarcity	kg Cu eq	-0.0370	-0.0623	-0.0287	**53.9 %**	**40.7 %**
Fossil resource scarcity	kg oil eq	0.5	8.2	4.4	**-46.3%**	**-93.8%**

Figure 5.2.12 and Table 5.2.4 show the results of the sensitivity analysis on the variation of P_2O_5 content in the sludge used to produce SSA which are used by the PARFORCE process. Given the very low P_2O_5 loss during incineration, the variation in P_2O_5 content of sludge can be directly related to the variation in P_2O_5 content of ash from incineration. Here again, the influence of P_2O_5 variation in the sludge on the process was discussed with a process holder. Only the impact of a +30% variation in sludge content was assessed due to the technical limitations of the data set available for this process. The results show that an increase in the P_2O_5 content of the sludge leads to an increase in the environmental impacts of the system. This can be explained by the fact that acid and heat consumption increase when the P_2O_5 content of the ash used increases. The increase in phosphorus recovery in the SSA is considered to be linear. The positive influence of this variation on the environmental impact of mineral resource depletion is however clearly visible.

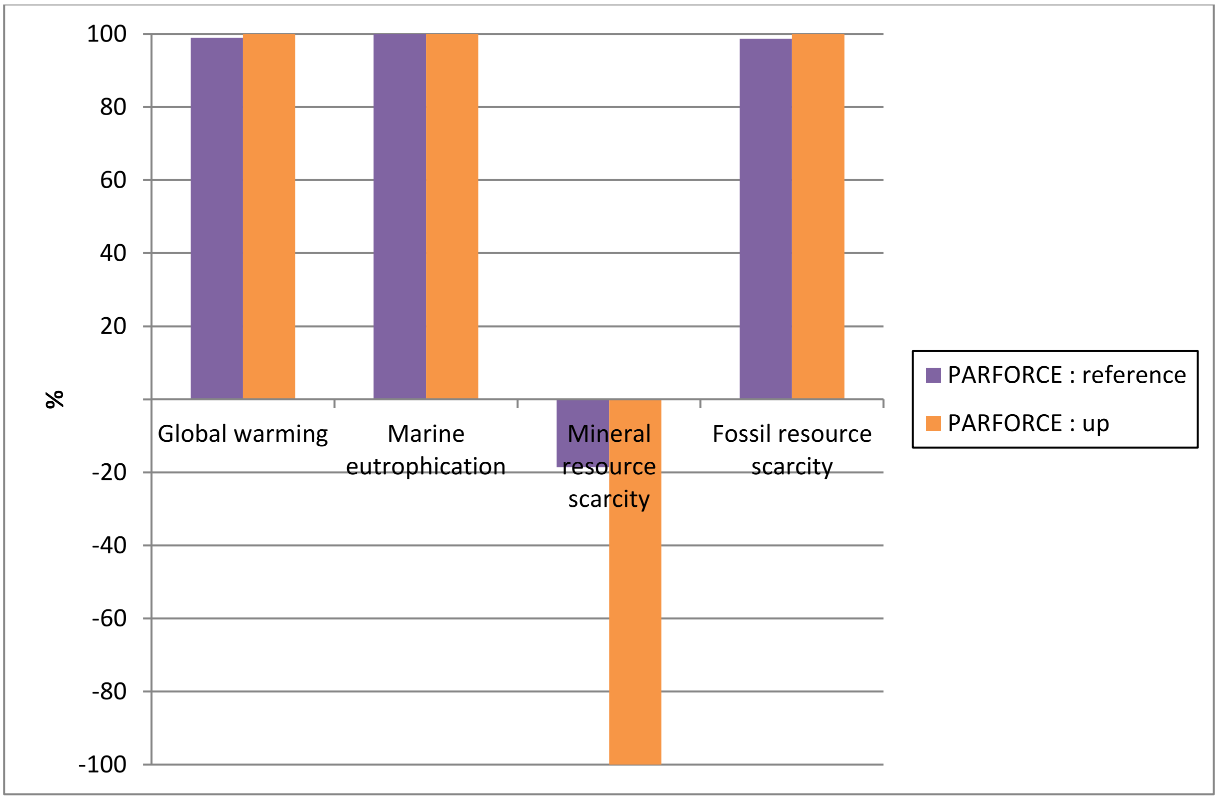


Figure 5.2.12: Comparison of the environmental impacts of the PARFORCE system for the two levels of P_2O_5 content in the digested sludge studied – Characterisation ReCiPe 2016 H/World H

Table 5.2.4: Sensitivity analysis of the environmental impacts of the PARFORCE system for a +30% variation P_2O_5 content in sludge

Impact category	Unit	PARFORCE: up	PARFORCE: reference	**Difference: reference - up**
Global warming	kg CO_2 eq	32.1	31.8	**1.0 %**
Marine eutrophication	kg N eq	0.09304	0.09307	**-0.033 %**
Mineral resource scarcity	kg Cu eq	-0.154	-0.029	**-437.9 %**
Fossil resource scarcity	kg oil eq	4.5	4.4	**1.3 %**

5.2.2.4 *LCA of the Struvia™ recovery system*

Introduction

The system boundaries studied in the case of the Struvia™ demonstrator with the avoided burden method are similar to those explained in the case of the system expansion method. These boundaries include the WWTP, the Struvia™ process itself as well as the biodigestion and cogeneration phases (in which the input of easily biodegradable co-products has been taken into account) as well as the incineration with energy recovery and the landfill of the incineration residues. It was estimated that the Struvia™ process could produce 0.26 kg of P_2O_5 from the 305.6 kg of sludge at DM 5 % from the treatment of 100 m^3 of wastewater. This production was taken into account as avoided TSP production, so the corresponding amount is 0.54 kg TSP (at 48 % P_2O_5).

Figure 5.2.13 shows the boundaries of the system under study.

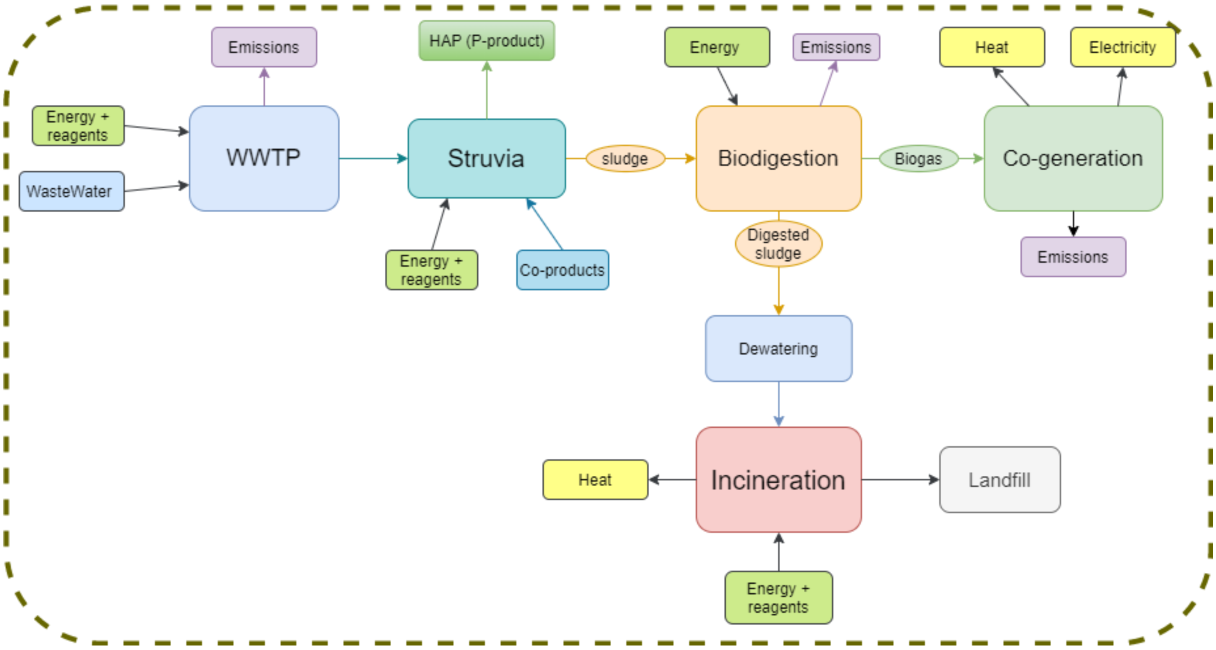


Figure 5.2.13: System boundaries for the Struvia system with the avoided burden approach

Results of Struvia™ system

Figure 5.2.14 shows the results of the environmental impacts of the Struvia™ system with the avoided burden method. These results are comparable to those obtained with the system expansion method. The WWTP is responsible for most of the environmental impacts (in orange). The sludge dewatering stage (in brown) is also responsible for significant impacts on the categories of mineral and fossil resource depletion and global warming. The beneficial effects of cogeneration (yellow) and incineration with energy recovery (light blue) are also visible on the categories of fossil resource depletion and global warming. The avoided production of TSP (dark blue) is responsible for a significant environmental benefit in the category of mineral resource depletion.

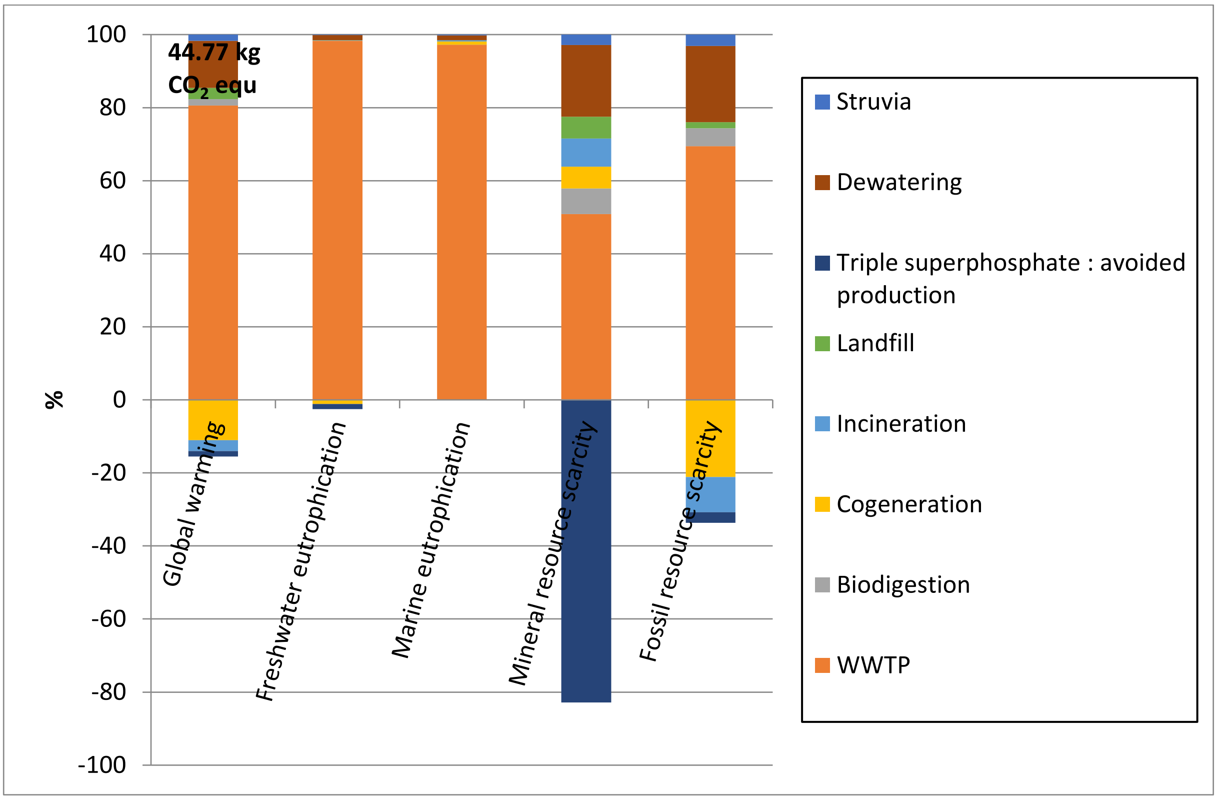


Figure 5.2.14: Environmental impacts of the Struvia™ system with the avoided burden approach – Characterisation ReCiPe 2016 H/World H

Figure 5.2.15 shows the comparison of the impacts of the Struvia™ system and the reference system for the avoided burden method. The conclusions drawn earlier with the system expansion method are confirmed. The impacts of the Struvia™ system appear to be lower for the categories of global warming and fossil fuel depletion. The impacts of the Struvia™ system on the mineral depletion category are much lower than those of the reference system.

The differences in the climate change and eutrophication categories do not reach the significance level (10 and 30% respectively), while the differences in the other categories (depletion of fossil resources: 10% and mineral resources: 30%) do.

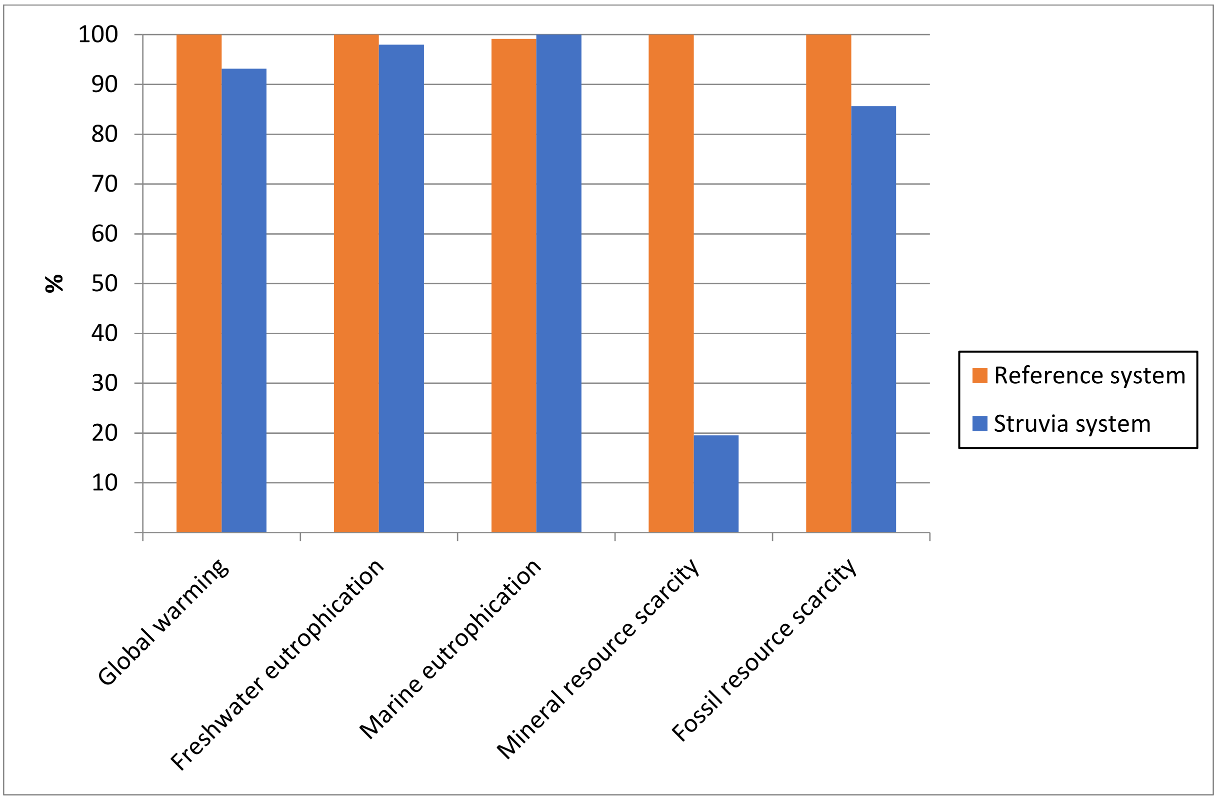


Figure 5.2.15: Comparison of the environmental impacts of the Struvia™ system and the reference system with the avoided burden method – Characterisation ReCiPe 2016 H/World H

Figure 5.2.16 and Table 5.2.5 present the results of the sensitivity analysis on the origin of the electricity mix used in the modelling. As for the other systems, the impacts of the system using German electricity are more important than the one using French electricity. The impacts of the system using Belgian electricity are at intermediate levels between the two previous ones.

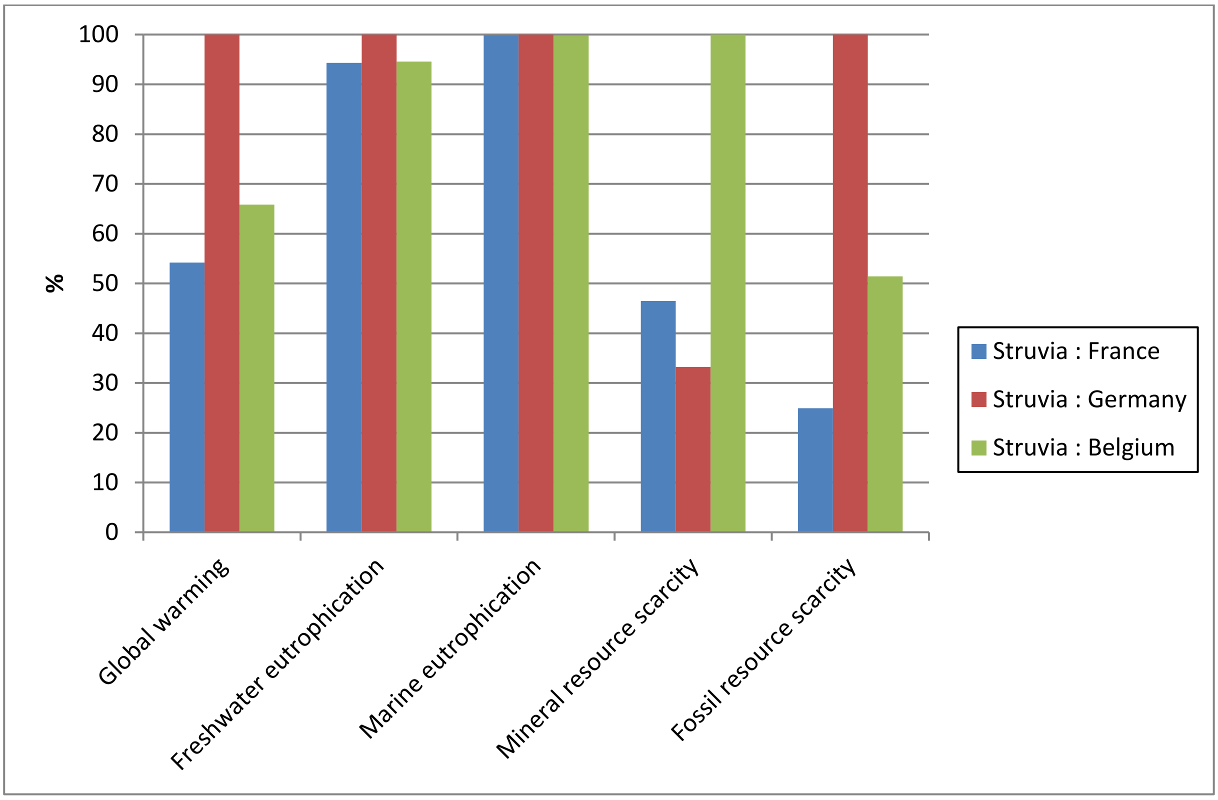


Figure 5.2.16: Comparison of the environmental impacts of the Struvia system for the three electricity mixes studied (German, Belgian and French)– Characterisation ReCiPe 2016 H/World H

Table 5.2.5: Sensitivity analysis of the environmental impacts of the Struvia™ system for the three electricity mixes studied (German, Belgian and French)

Impact category	Unit	Struvia™: France	Struvia™: Germany	Struvia™: Belgium	**Difference: Germany - Belgium**	**Difference: Germany - France**
Global warming	kg CO_2 eq	24.2	44.8	29.5	**-34.2 %**	**-45.8 %**
Freshwater eutrophication	kg P eq	0.0574	0.0609	0.0576	**-5.5 %**	**-5.7 %**
Marine eutrophication	kg N eq	0.0939	0.0941	0.0939	**-0.1 %**	**-0.2 %**
Mineral resource scarcity	kg Cu eq	0.0202	0.0144	0.0434	**201.2 %**	**39.9 %**
Fossil resource scarcity	kg oil eq	1.6	6.5	3.4	**-48.6 %**	**-75.1 %**

A sensitivity analysis was performed on the P_2O_5 content of the sludge used in the Struvia™ process. For this purpose, two variations of plus and minus 30 % of the P_2O_5 content of the final P-material were studied. The reference cases are a P-material with 16 % P_2O_5 and a quantity of 0.26 kg of P_2O_5 recovered from the 305.6 kg of sludge at DM 5 %. The low case corresponds to a final product with 11.2 % P_2O_5 and a quantity of 0.18 kg P_2O_5 recovered. The high case corresponds to 20.8 % P_2O_5 in the final product and 0.34 kg P_2O_5 recovered.

Figure 5.2.17 and Table 5.2.6 illustrate the results of this sensitivity analysis. The environmental impacts of the different cases do not vary significantly for the categories of global warming, eutrophication and fossil resource scarcity. However, the variation in P_2O_5 content has a strong impact on the mineral resource scarcity category. The impact on this category increases sharply when the phosphorus content drops.

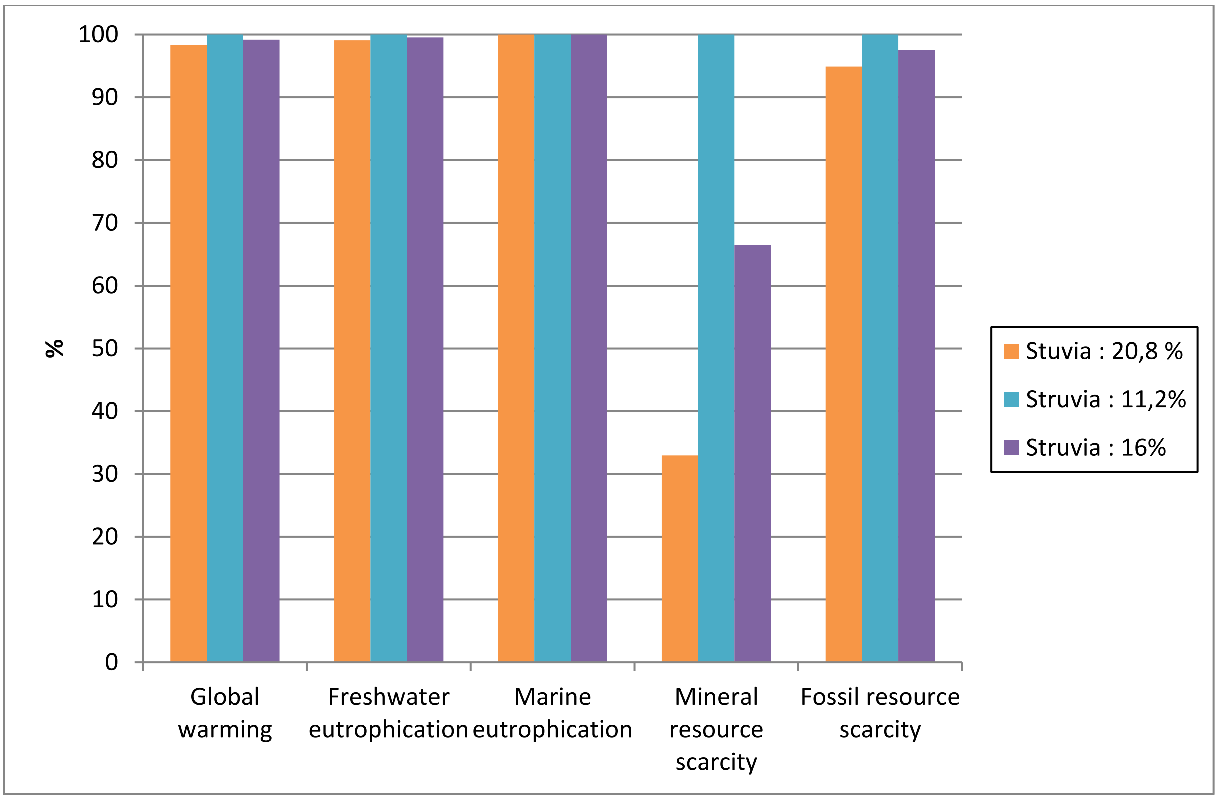


Figure 5.2.17: Comparison of the environmental impacts of the Struvia™ system for the three levels of P_2O_5 content studied in the sludge – Characterisation ReCiPe 2016 H/World H

Table 5.2.6: Sensitivity analysis of the environmental impacts of the Struvia™ system for the three levels of phosphorus content studied

Impact category	Unit	Struvia™: 20,8 %	Struvia™: 11,2%	Struvia™: 16%	**Difference: reference - down**	**Difference: reference - up**
Global warming	kg CO_2 eq	24.2	44.8	29.5	**51.9 %**	**-17.7 %**
Freshwater eutrophication	kg P eq	0.0574	0.0609	0.0576	**5.8 %**	**-0.2 %**
Marine eutrophication	kg N eq	0.0939	0.0941	0.0939	**0.15 %**	**-0.02 %**
Mineral resource scarcity	kg Cu eq	0.0202	0.0144	0.0434	**66.8 %**	**-53.6 %**
Fossil resource scarcity	kg oil eq	1.6	6.5	3.4	**94.5 %**	**-51.5 %**

5.2.2.5 *LCA of the PULSE recovery system*

Introduction

The principle of the PULSE process is the direct treatment of dried sludge by acid leaching followed by the solvent extraction of metals and the precipitation of phosphorus-rich PULSE product.

The system containing the PULSE process also contains the WWTP, the biodigestion with cogeneration with the biogas, the treatment of the digested sludge by the PULSE process itself (including preliminary drying) and finally the incineration of the residual sludge with energy recovery. The drying of the sludge used in the PULSE process was modelled using the consumption of an industrial scale dryer (natural gas powered) in order not to bias the results. The PULSE process produces 0.72 kg of P_2O_5 from the 60.57 kg produced by the 100 m³ treatment. This amount of P_2O_5 corresponds to an avoided production of TSP (at 48 %) of 1.56 kg.

Figure 5.2.18 presents the boundaries of the PULSE case.

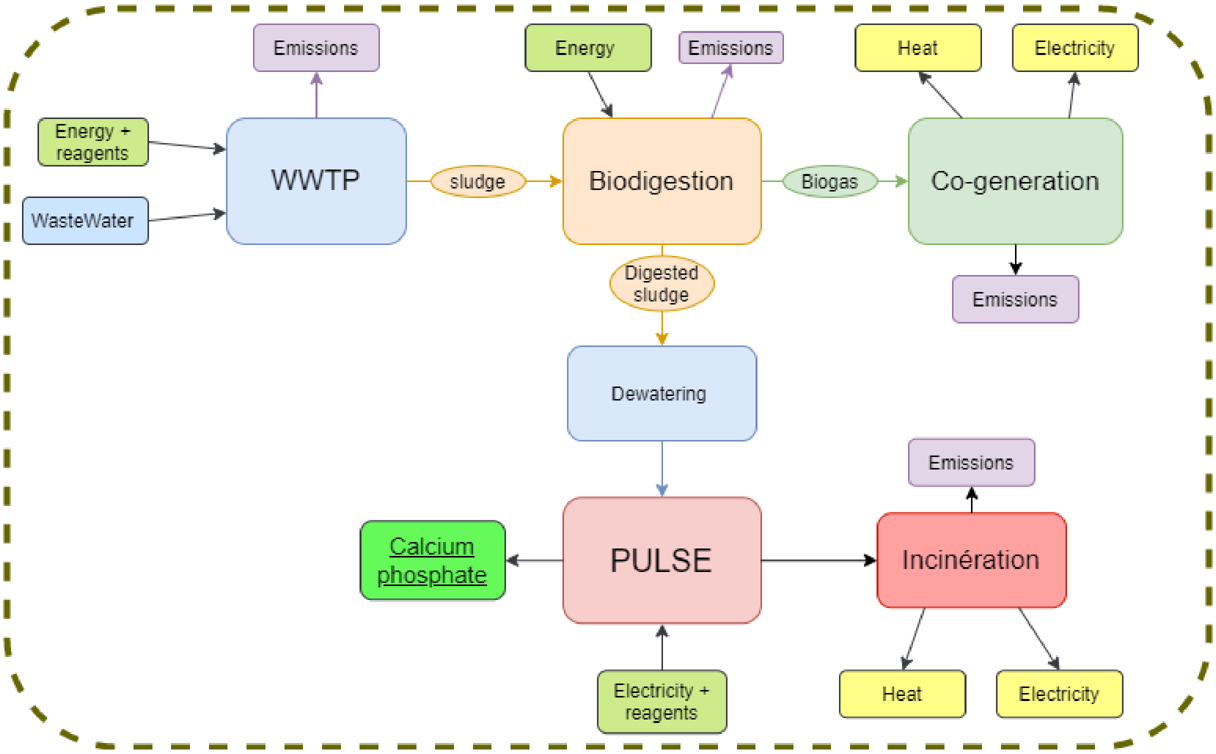


Figure 5.2.18: System boundaries for the Pulse system with the avoided burden approach

Results of the PULSE system

The results below show the importance of the environmental impacts of the PULSE process itself (in blue) on the categories of global warming, depletion of fossil and mineral resources. Logically, the avoidance of chemical fertilizer production has a significant beneficial effect on mineral resource depletion (dark blue).

Figure 5.2.19 presents the results of the PULSE case.

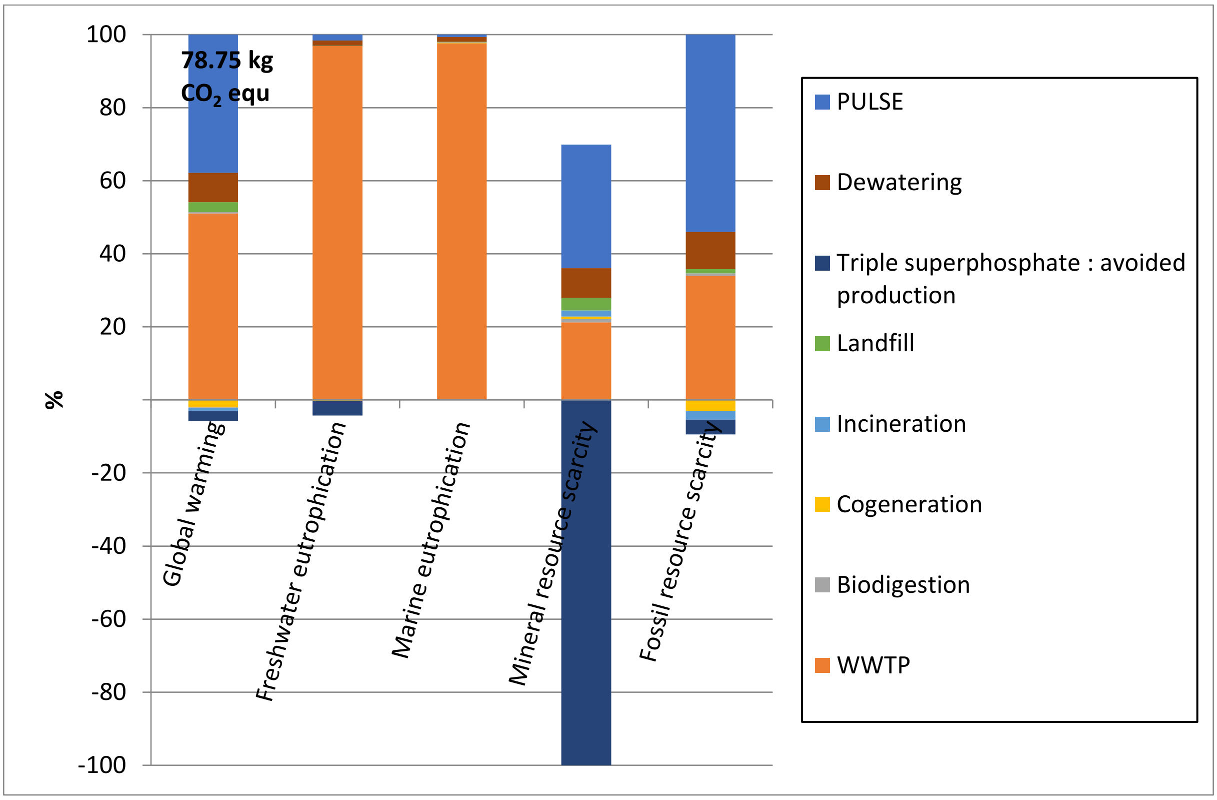


Figure 5.2.19: Environmental impacts of the PULSE system with the avoided burden approach – Characterisation ReCiPe 2016 H/World H

Figure 5.2.20 displays the comparison of the environmental impacts of the PULSE system and the reference system. As was already the case when applying the system extension method, the impacts of the PULSE system are greater than those of the reference case in all categories except in the category of mineral resource scarcity. In this category, the impact of the reference system is larger.

The observed differences are significant for the categories of global warming, fossil and mineral resource scarcity.

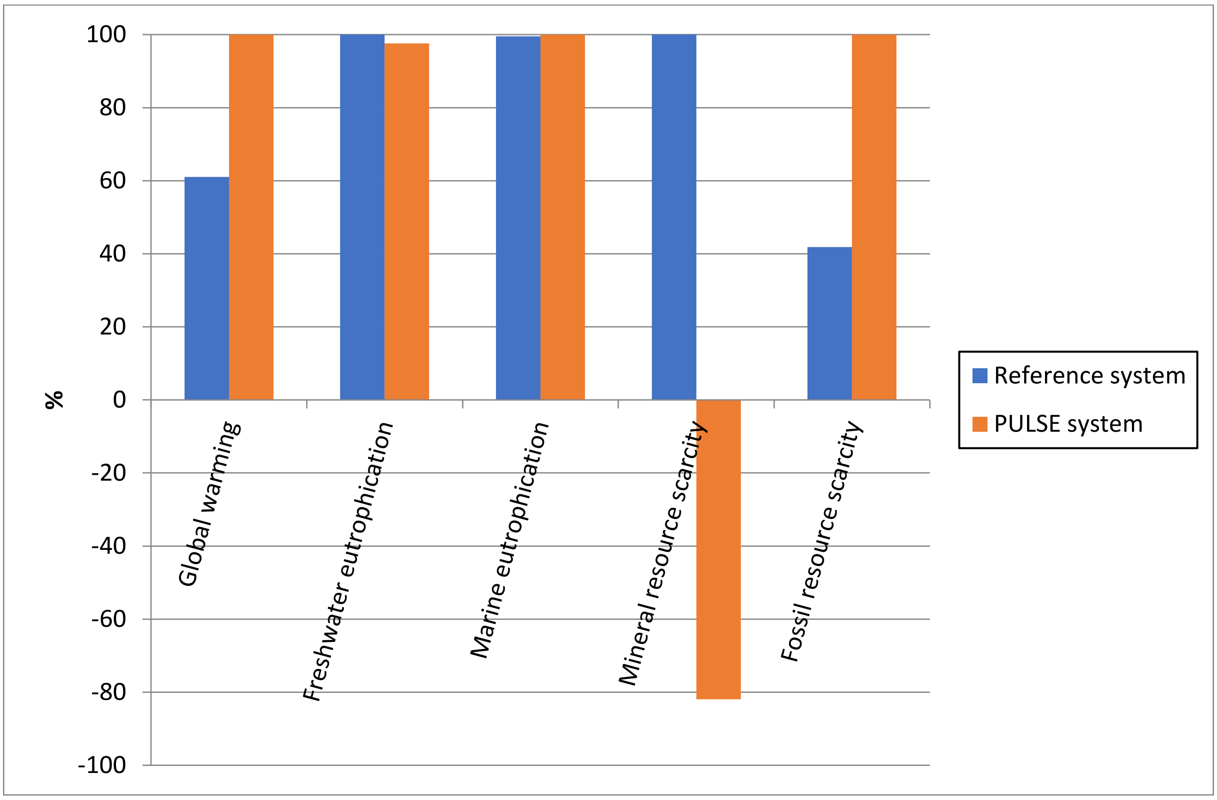


Figure 5.2.20: Comparison of the environmental impacts of the PULSE system and the reference system with the avoided burden method – Characterisation ReCiPe 2016 H/World H

Figure 5.2.21 and Table 5.2.7 present the results of the sensitivity analysis of the PULSE system with respect to the origin of the electricity used. As for other systems, the environmental impact of the system using German electricity is globally greater than that using Belgian electricity, which are themselves higher than those of the system using French electricity.

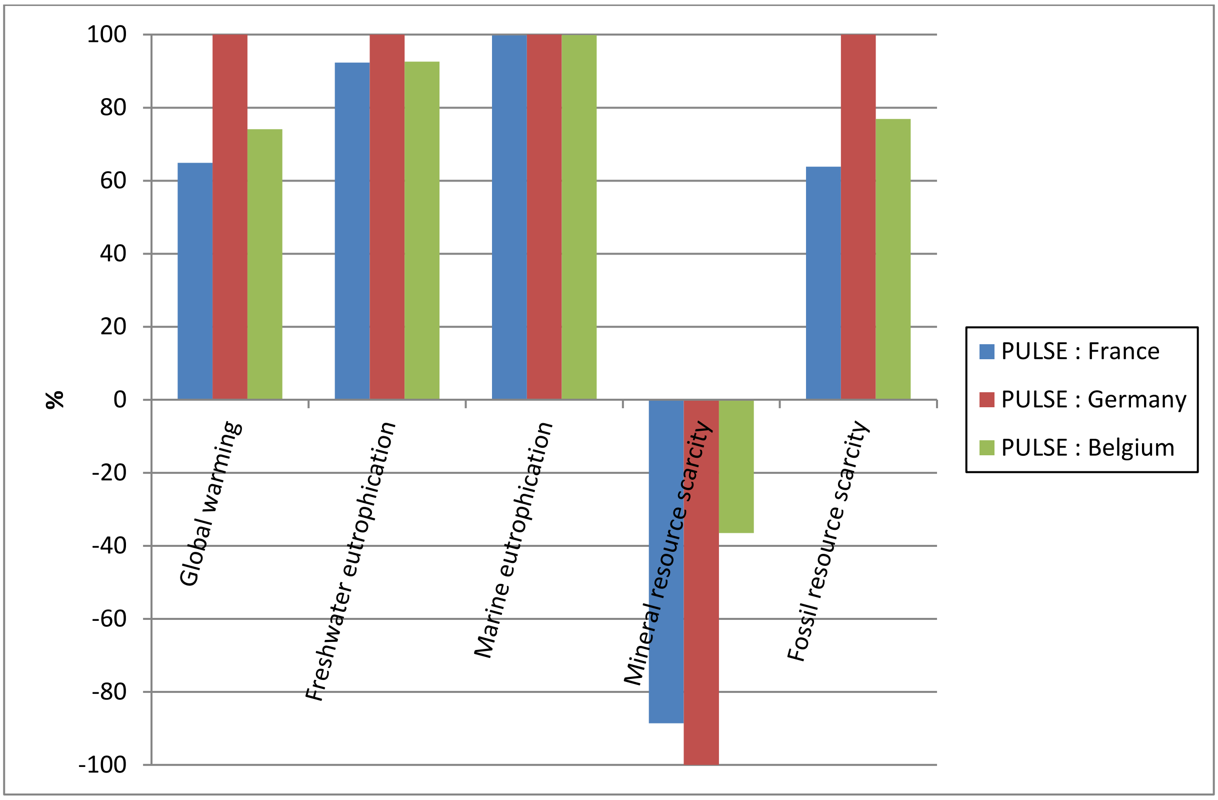


Figure 5.2.21: Comparison of the environmental impacts of the PULSE system for the three electricity mixes studied (German, Belgian and French) – Characterisation ReCiPe 2016 H/World H

Table 5.2.7: Sensitivity analysis of the environmental impacts of the PULSE system for the three electricity mixes studied (German, Belgian and French)

Impact category	Unit	PULSE: France	PULSE: Germany	PULSE: Belgium	**Difference: Germany - Belgium**	**Difference: Germany - France**
Global warming	kg CO_2 eq	51.1	78.8	58.3	**-26.0 %**	**-35.2 %**
Freshwater eutrophication	kg P eq	0.0560	0.0607	0.0562	**-7.4 %**	**-7.7 %**
Marine eutrophication	kg N eq	0.0935	0.0937	0.0935	**-0.17 %**	**-0.19 %**
Mineral resource scarcity	kg Cu eq	-0.0536	-0.0605	-0.0221	**63.5 %**	**11.4 %**
Fossil resource scarcity	kg oil eq	11.6	18.2	14.0	**-23.1 %**	**-36.1 %**

Figure 5.2.22 and Table 5.2.8 present the results of the sensitivity analysis of the PULSE system with respect to the P_2O_5 content in the sewage sludge used. For the PULSE process, only the P_2O_5 content in the finished P-material varies linearly with the P content of the sewage sludge used. The cases evaluated consist of a low case at minus 30 % and a high case at plus 30 %. In the reference case, the process recovers 0.63 kg of P_2O_5 (P_2O_5 content: 27 %), in the low case it recovers 0.44 kg (P_2O_5 content: 18.9 %) and in the high case it recovers 0.82 kg (P_2O_5 content: 35.1 %). The process consumptions have also been adapted linearly.

As the results show, the influence of the variation in P_2O_5 of the sewage sludge is significant only on the category of depletion of mineral resources.

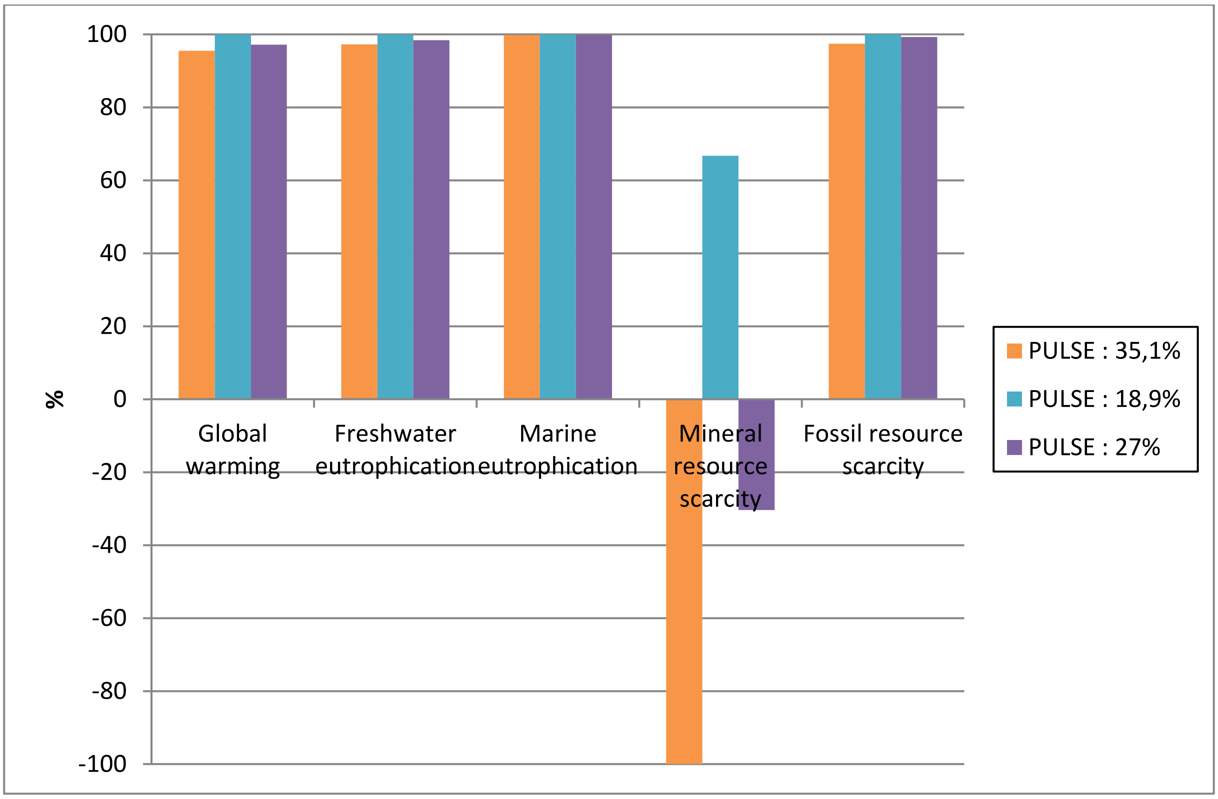


Figure 5.2.22: Comparison of the environmental impacts of the PULSE system for the three levels of P_2O_5 content studied in the sludge – Characterisation ReCiPe 2016 H/World H

Table 5.2.8: Sensitivity analysis of the environmental impacts of the PULSE system for the three levels of P_2O_5 content studied in the sludge

Impact category	Unit	PULSE: 35,1%	PULSE: 18,9%	PULSE: 27%	**Difference: reference - down**	**Difference: reference - up**
Global warming	kg CO_2 eq	57.3	60.0	58.3	**2.9 %**	**-1.7 %**
Freshwater eutrophication	kg P eq	0.0556	0.0571	0.0562	**1.7 %**	**-1.1 %**
Marine eutrophication	kg N eq	0.0935	0.0937	0.0935	**0.12 %**	**-0.05 %**
Mineral resource scarcity	kg Cu eq	-0.0728	0.0486	-0.0221	**319.9 %**	**-229.3 %**
Fossil resource scarcity	kg oil eq	13.8	14.1	14.0	**0.8 %**	**-1.8 %**

5.2.3 Discussion of results for LCA with avoided burden approach

The environmental analysis performed with the avoided burden approach confirmed the findings of the analysis performed with the system expansion approach. The differences in environmental impacts between the two methodological approaches are fairly small, which increases the robustness of the conclusions drawn from these analyses.

The sensitivity analysis on the electricity mix used in the system modelling showed that generally the use of the German electricity mix leads to higher impacts on the fossil fuel depletion and climate change categories due to the use of fossil fuels for electricity generation. On the other hand, the use of the German electricity mix has a lower impact on the category of mineral resource depletion, which can be explained by the lower use of nuclear power.

Finally, the sensitivity analysis performed on the P_2O_5 content of the sludge used in the different systems showed that this variation had mainly an effect on the impact of the mineral resource depletion category.

5.3 LCC analysis

In order to complete the evaluation of the recovery processes, a cost analysis would be useful to assess the economic qualities of the processes. This analysis can take the form of a life cycle cost analysis (LCC), which consists of summing all the flows into the system and subtracting all the flows out. In the case of P-recovery technologies, the main monetary flows are the APEX, the OPEX, and flows related to the sludge exchange, the staff, the waste management and the phosphorus fertiliser itself. This principle of cost analysis is illustrated in the Figure 5.3.1.

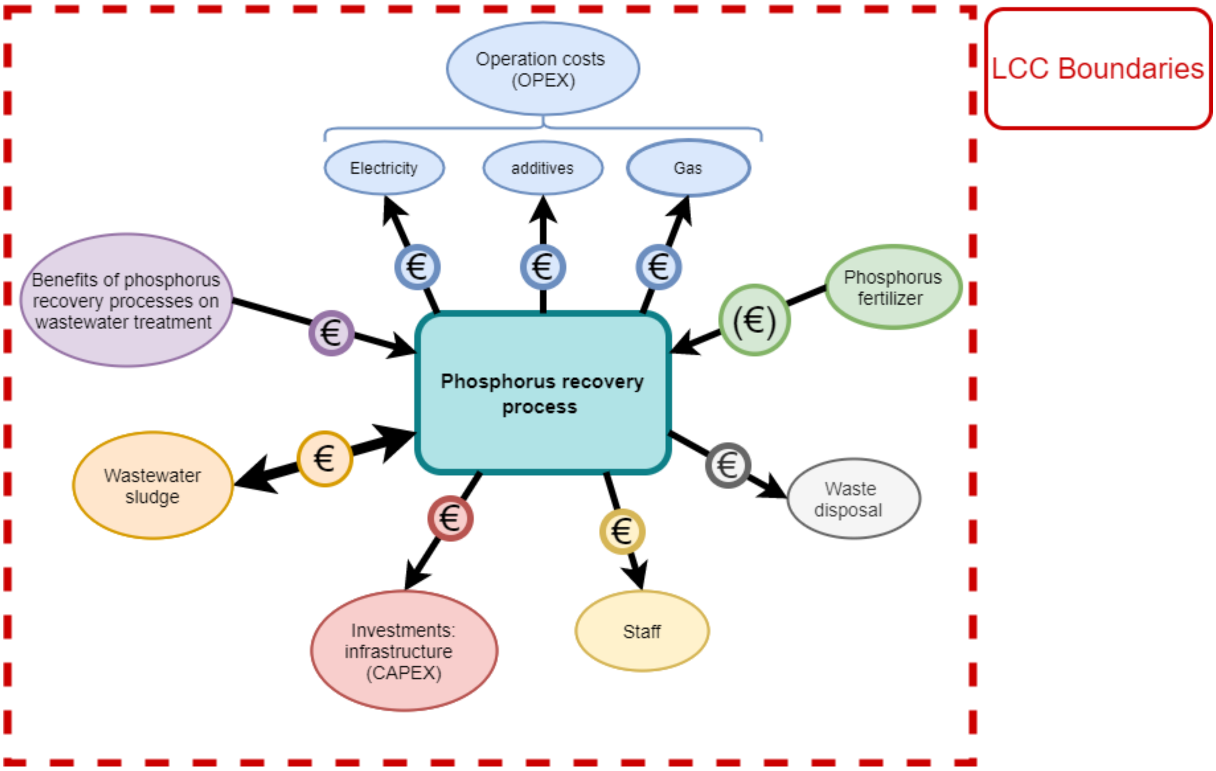


Figure 5.3.1: Illustration of the principle of life cycle costing as applied to P-recovery technologies

Such an analysis is only possible with the collaboration of the owners of the P-recovery technologies, which ensures an exchange of the data needed for the cost analysis. Once this data is received, cost analyses are carried out to determine two key factors. The first is the cost of production of the P-material by the demonstrator (in €/kg P_2O_5). The second is the cost of the treatment of one tonne of sludge by the recovery process (€/tonne of treated sludge).

For reasons of data availability and small scale, only the costs of the EuPhoRe® process are analysed.

5.3.1 LCC analyses of EuPhoRe® process

The data used for the cost analysis of the EuPhoRe® process comes directly from process owner and corresponds to the treatment of 5,200 tonnes of solar dried DM 75 % sludge per year and an annual production of 306 tonnes of P_2O_5. It is important to keep in mind that these costs are not fixed and can vary from year to year.

Table 5.3.1 shows the data.

Table 5.3.1: Financial data for the EuPhoRe® process

Costs	
Electricity	101.000,00 €
License fee, insurance and maintenance	150.000,00 €
Additives	44.000,00 €
Gas	15.000,00 €
Staff	120.000,00 €
Investment : infrastructure	702.000,00 €
Gas processing	25.000,00 €
Residual product from gas purification	15.000,00 €
Benefits	
P-material	18.000,00 €
Thermal energy	600.000,00 €
CO_2 certificates	100.000,00 €

The annual amortisation was calculated over ten years and with an interest rate of 3 %, in line with what was done in the European P-REX project.

Figure 5.3.2 shows the cost distribution of the EuPhoRe® process.

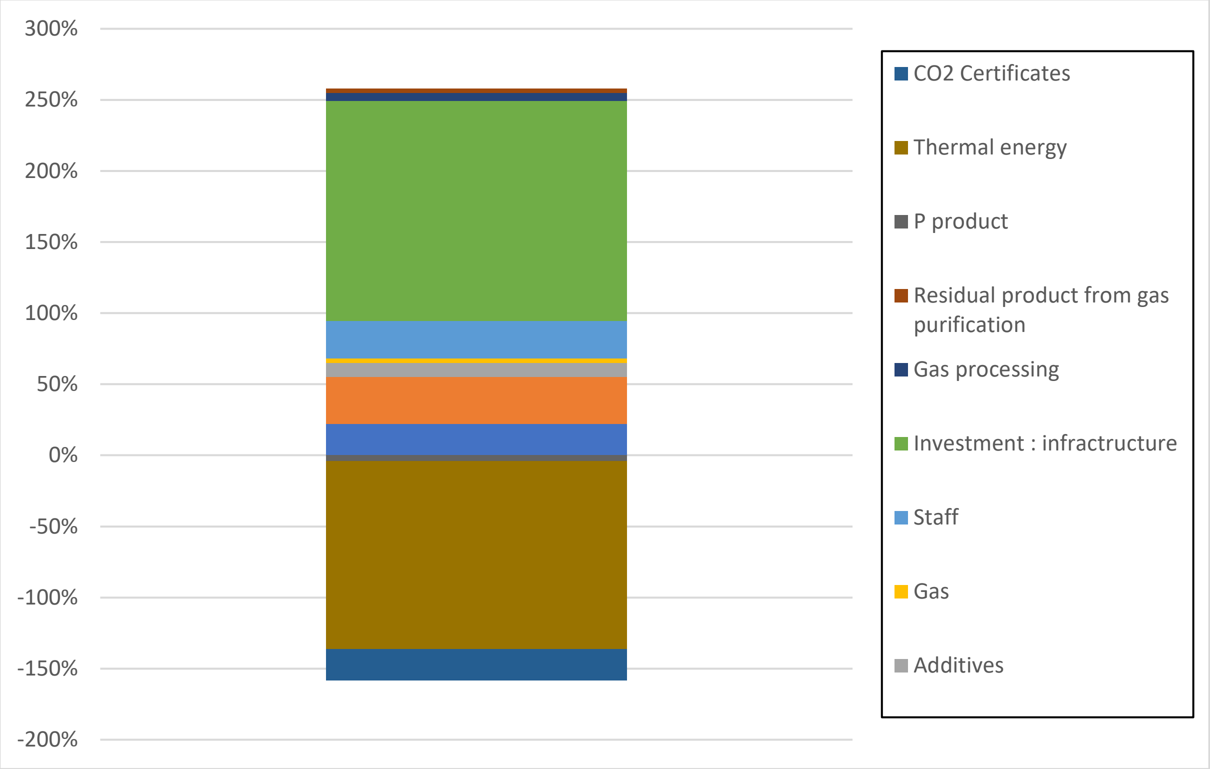


Figure 5.3.2: Repartition of costs for EuPhoRe® process

This distribution shows that the investments for the infrastructure represent the majority of the expenses and that the thermal energy resold is the main source of income of the process and concerns sewage sludge disposal including phosphorus recycling.

The selling price of the P-material produced by the EuPhoRe process taken into account in this study is 0.05 €/ kg P_2O_5. This value seems low compared to the selling price of TSP from imported phosphate rock which is estimated at 0.87 €/kg of P_2O_5 (European Commission 2021). However, the grinding and dust binding of the local production of EuPhoRe® must still be taken into account.

Finally, the cost of the treatment of one tonne of sewage sludge (in dry matter) could also be calculated. This cost amounts to 115 - 120 €/tonne DM for treatment of solar dried sewage sludge with the EuPhoRe® process. Solar drying costs 20 – 25 €/tonne DM. (Roskosch et al. 2018). That is the sum total of 135 – 145 € for this special application (solar dryer and EuPhoRe® process). It is interesting to compare this cost to the reference scenario used during the environmental analysis, the incineration of dewatered sludge (without drying step). The cost of incineration of dewatered sludge is estimated between 200€/tonne DM and 400€/tonne DM (Đurđević et al. 2019). The

EuPhoRe® system studied here seems therefore to show an economic advantage as a way to valorise sewage sludge, in addition to the obvious advantage of local production of P-material through the recycling of the phosphorus found in the treated sludge.

5.4 Conclusion of LCA-LCC works

The results of the analysis of the environmental performance of the systems including the recovery processes showed that all processes had an environmental advantage in terms of the mineral resource depletion category. This advantage reflects the possibility of saving the world's mineral resources and more specifically phosphorus. A major advantage of these demonstrators is that they prove that the made in Europe production of phosphorus is feasible and well within reach. This production will reduce Europe's dependence on phosphorus importing countries. The European food production system will then be less sensitive to possible geopolitical conflicts with these importing countries.

Some demonstrators such as EuPhoRe® and Struvia™ have also shown their potential beneficial effects on other studied categories such as climate change and fossil fuel depletion.

Two methodological approaches were studied in the environmental analysis of the demonstrators, the system extension approach and the avoided burden approach. Both approaches showed similar results and led to similar conclusions.

Finally, it is important to remember some key assumptions of the environmental analysis of the project demonstrators. Firstly, the P-materials from the demonstrators were considered legally usable. These products were therefore put on an equal footing even though they may differ in terms of purity and concentration (and bioavailability). Possible traces of pollutants, such as heavy metals, were not taken into account, nor were other nutrients possibly present in the P-materials.

The cost analysis (LCC) of the EuPhoRe® process showed that the production of one kilogram of P_2O_5 by the process was more expensive than the purchase price of P_2O_5 from phosphate rock (70 % price increase). However, this price difference should be seen in the light of the advantages of local, sustainable and independent production at European level. It has also been shown that the price of sludge disposal via the EuPhoRe® process can be lower than that of conventional incineration. Therefore, the process has an economic advantage as a means of sludge valorisation.

6 Outlook

Seven processes to recover phosphorus from municipal wastewater were demonstrated in real environment within the Phos4You project. All demonstrators were technically successful in producing phosphorus materials from wastewater, WWTP effluents, sewage sludge or sewage sludge ashes.

Except the phosphoric acid being a common chemical substance, the generated samples of materials were made available to research institutions and universities for the assessment of their fertilising quality. Those works are reported in a dedicated report (Bogdan et al. 2021) The samples of those recovered materials were also made available to industrial partners, in order to test their suitability to be integrated in their production processes.

The results of the technical proofs of concept delivered baseline information for the development of scenarios and case studies to implement the phosphorus recycling in urban and rural regions. The details of those works are presented in the final report of the Phos4You partnership (Ploteau et al. 2021).

As a whole, the project confirmed that the diversity of P-recovery solutions proposed allow to cover a wide range of configuration: from very small wastewater systems to highly complex treatment including incineration of sewage sludge). Nevertheless, by the development of scenarios based on the Phos4You demonstrations, it was showed that the choice of an appropriated P-recovery solution needs to undergo a complex decision-making process.

On the one hand, the selected technology needs to fit with the current situation. The development of wastewater treatment in Europe has resulted in a successive addition of treatment steps (preliminary treatment, primary treatment, secondary or biological treatment and tertiary or advanced treatment) in order to face the new emerging problems. The P-recovery creates an additional step. By selecting a technology, the cycle of investment of the different parts of the treatment system need to be considered, rendering in some case difficult to implement a more holistic approach which would require a global system change (e.g. in case of algae solutions or new way to incinerate sludge).

On the other hand, the selected technology needs to meet the requirements of the future situation and its related objective. The EU set up a “zero pollution” vision at horizon 2050 “to respect the boundaries our planet can cope with” (European Commission 2020c). This is fully in line with the key-findings of the Intergovernmental

Panel on Climate Change calling in its report 2021 for “deep reductions in CO_2 and GHG emissions” (IPCC 2021). This opens discussion on future adapted valorisation and treatment of sewage sludge, rendering thereby difficult the selection of a long-term P-recovery solution.

The level of transnational cooperation is a further criterion by the selection of a P-recovery solution. Through the cross-border activities between Phos4You partners and stakeholders of the fertiliser sector, it became evident that the transnational cooperation in the field of P-recovery is slow-down by the complex rules of the EU related to the transport of waste materials. The notification procedure applying for very small quantities of material renders some simple testing disproportionally labour- and cost-intensive (e.g. in case of transport of sewage sludge ashes). This is not encouraging cooperation for full-scale P-recycling.

The evaluation of the Phos4You demonstrations showcased how the implementation of P-recovery technologies enlarges the field of activities waterboards are dealing with. Consequently, new staff competences will be required for the operation and management of P-recovery plants. Where large streams of materials such as chemicals, products, by-products and input materials will flow, the logistical aspects of the P-recycling will gain in strategical importance.

Overall, the benefits of development centres at wastewater treatment plants for emerging technologies has been stated. Those facilities enabled for easier set up and operation of Phos4You demonstrators (e.g. Bo´Ness (Scotland), Technikum/Dinslaken (Germany)) in comparison with the Phos4You demonstrators installed at standard wastewater plants. This was particularly true in term of authorisation procedure, technical installation and access under pandemic condition.

The environmental assessment of the recovery technologies highlighted the most damaging parts of each process and demonstrated case by case their environmental impacts. This assessment also enabled the comparison of two methodological approaches to solve the thorny problem of taking into account the WWTP in the LCA of recovery technologies (system expansion method and avoided burden method). Both approaches provided comparable results, which reinforces their robustness for the application to the process of phosphorus recovery from sewage sludge. Considering this robustness, international standardisation norms such as the ILCD Handbook and the EPD could require the application of one of these methodological approaches in the environmental assessment of wastewater sludge-based fertilisers. This requirement would allow a homogenisation of methodological approaches in LCA studies of sludge-sourced fertilisers. This would facilitate the comparison of results to clearly highlight the individual environmental advantages of each recovery technology on a scientific basis.

The different P-recovery processes demonstrated in Phos4You will continue to be upscaled and implemented.

References

Aslan, Sebnem; Kapdan, Ilgi Karapinar (2006): Batch kinetics of nitrogen and phosphorus removal from synthetic wastewater by algae. In *Ecological Engineering* 28 (1), pp. 64–70. DOI: 10.1016/j.ecoleng.2006.04.003.

AWEL, Baudirektion des Kantons Zürich - Amt für Abfall, Wasser, Energie und Luft (2018) (Projektblatt, 6). Available online at https://zar-ch.ch/fileadmin/user_upload/Contentdokumente/Phosphor/projektblatt_phosphor_klaerschlammasche_nr_6.pdf, checked on 6/25/2021.

Bareha, Y.; Saoudi, M.; Santellani, A. C.; Le Bihan, A.; Picard, S.; Mebarki, C. et al. (2020): Use of fermentation processes for improving the dissolution of phosphorus and its recovery from waste activated sludge. In *Environmental technology*, pp. 1–11. DOI: 10.1080/09593330.2020.1827301.

Bednarz, Andreas; Rüngeler, Bettina; Pfennig, Andreas (2014): Use of Cascaded Option Trees in Chemical-Engineering Process Development. In *Chemie Ingenieur Technik* 86 (5), pp. 611–620. DOI: 10.1002/cite.201300115.

Bhatnagar, Ashish; Chinnasamy, Senthil; Singh, Manjinder; Das, K. C. (2011): Renewable biomass production by mixotrophic algae in the presence of various carbon sources and wastewaters. In *Applied Energy* 88 (10), pp. 3425–3431. DOI: 10.1016/j.apenergy.2010.12.064.

Blöhse, Dennis; Herr, Patrick (2018): Acid extraction of phosphorus from sewage sludge incineration ash: REMONDIS TetraPhos® (Phos4You Information sheet). Available online at https://www.nweurope.eu/media/5064/2_phos4you-tetraphos.pdf.

Blöhse, Dennis; Herr, Patrick (2019): Results of Pilot Scale Tests for P-Recovery from Emschergenossenschaft-Lippeverband Sewage Sludge Ashes with REMONDIS TetraPhos® Process. In Université de Liège (Ed.): Proceedings. 5th European Conference on Sludge Management Liège. Liège, 6-8 October.

Blöhse, Dennis; Ploteau, Marie-Edith; Schmelz, Karl-Georg; Nafo, Issa (2018): Konzepte eines großen Klärschlammerzeugers aus NRW zur Phosphorrückgewinnung: Erste Erkenntnisse aus dem INTERREG Verbundprojekt Phos4You. In Olaf Holm, Elisabeth Thomé-Kozmiensky, Peter Quicker, Stefan Kopp-Assenmacher (Eds.): Verwertung von Klärschlamm. Neuruppin: Thomé-Kozmiensky Verlag GmbH.

Bogdan, Aleksandra; Robles-Aguilar, Ana Alejandra; Szabolcs, Papp; Taggart, Mark; Coquery, Marina; Le Guédard, Marina et al. (2021): Quality assessment of recovered phosphorus materials carried out within the Phos4You project. Edited by Evi Michels, Erik Meers. UGhent. Ghent.

Braak, Etienne; Auby, Sarah; Piveteau, Simon; Guilayn, Felipe; Daumer, Marie-Line (2016): Phosphorus recycling potential assessment by a biological test applied to wastewater sludge. In *Environmental technology* 37 (11), pp. 1398–1407. DOI: 10.1080/09593330.2015.1116612.

Bunce, Joshua T.; Ndam, Edmond; Ofiteru, Irina D.; Moore, Andrew; Graham, David W. (2018): A Review of Phosphorus Removal Technologies and Their Applicability to Small-Scale Domestic Wastewater Treatment Systems. In *Front. Environ. Sci.* 6, p. 235. DOI: 10.3389/fenvs.2018.00008.

Chantrain, Gaspard (2021): Étude des impacts environnementaux de nouvelles technologies de récupération du phosphore dans les boues de station d'épuration. Master thesis for the grade of bio-engineer in environmental sciences and technologies. Université de Liège - Gembloux Agro-Biotech, Liège.

Chen, Zhijie; Zhang, Xinru; Jiang, Zeyi; Chen, Xuehui; He, Hongzhou; Zhang, Xinxin (2016): Light/dark cycle of microalgae cells in raceway ponds: Effects of paddlewheel rotational speeds and baffles installation. In *Bioresource Technology* 219, pp. 387–391. DOI: 10.1016/j.biortech.2016.07.108.

Cork County Council (2008): Wastewater Discharge Licence Application under S.I 684 of 2007 Regulations - Scheme/Agglomeration: Macroom - Submission Date: 22nd September 2008.

Cornel, P.; Schaum, C. (2009): Phosphorus recovery from wastewater: needs, technologies and costs. In *Water science and technology : a journal of the International Association on Water Pollution Research* 59 (6), pp. 1069–1076. DOI: 10.2166/wst.2009.045.

Cuaresma, María; Garbayo, Inés; Vega, José M.; Vílchez, Carlos (2006): Growth and photosynthetic utilization of inorganic carbon of the microalga Chlamydomonas acidophila isolated from Tinto river. In *Enzyme and Microbial Technology* 40 (1), pp. 158–162. DOI: 10.1016/j.enzmictec.2005.10.049.

Deng, Xiangyuan; Chen, Biao; Xue, Chunye; Li, Da; Hu, Xiaoli; Gao, Kun (2019): Biomass production and biochemical profiles of a freshwater microalga Chlorella kessleri in mixotrophic culture: Effects of light intensity and photoperiodicity. In *Bioresource Technology* 273, pp. 358–367. DOI: 10.1016/j.biortech.2018.11.032.

Deutscher Bundestag (2017): Verordnung zur Neuordnung der Klärschlammverwertung. (Klärschlammverordnung - AbfKlärV). Source: Bundesgesetzblatt Jahrgang 2017 Teil I (65), pp. 3465–3512. Available online at http://www.gesetze-im-internet.de/abfkl_rv_2017/index.html.

Doetsch, Peter; Pinnekamp, Johannes; Rath, Walter; Grömping, Markus (2010): Rückgewinnung von Pflanzennährstoffen, insbesondere Phosphor aus der Asche von Klärschlamm. Abschlussbericht PASCH. With assistance of David Montag. Edited by Umwelt-Forum der RWTH Aachen. Institut für Siedlungswasserwirtschaft der RWTH Aachen.

Đurđević, Dinko; Blecich, Paolo; Jurić, Željko (2019): Energy Recovery from Sewage Sludge: The Case Study of Croatia. In *Energies* 12 (10), p. 1927. DOI: 10.3390/en12101927.

Eirich GmbH & Co KG (2021): Versuchsbericht - Versuche vom Granulieren von Klärschlammasche (not published). Hardheim.

Escudero, Ania; Blanco, Fernando; Lacalle, Arrate; Pinto, Miriam (2014): Ammonium removal from anaerobically treated effluent by Chlamydomonas acidophila. In *Bioresource Technology* 153, pp. 62–68. DOI: 10.1016/j.biortech.2013.11.076.

Escudero, Ania; Hunter, Colin; Roberts, Joanne; Helwig, Karin; Pahl, Ole (2020a): Pharmaceuticals removal and nutrient recovery from wastewaters by Chlamydomonas acidophila. In *Biochemical Engineering Journal* 156, p. 107517. DOI: 10.1016/j.bej.2020.107517.

Escudero, Ania; Klose, Siegfried; Ploteau, Marie-Edith (2020b): Microalgae biomass (Phos4You Information sheet). Available online at https://www.nweurope.eu/media/12160/phos4you_microalgae_biomass_en_nov2020.pdf.

EU COM - DG Research and Innovation (2015): Circular approaches to phosphorus. From research to deployment. Luxembourg: Publications Office.

European Commission (2014): COM(2014) 297 final - On the review of the list of critical raw materials for the EU and the implementation of the Raw Materials Initiative.

European Commission (2017a): COM(2017) 490 final - On the 2017 list of Critical Raw Materials for the EU.

European Commission (2017b): Ninth Report on the implementation status and the programmes for implementation (as required by Article 17) of Council Directive 91/271/EEC concerning urban waste water treatment. COM/2017/0749 final.

European Commission (2019): SWD(2019) 700 final - Evaluation of the Council Directive 91/271/EEC of 21 May 1991, concerning urban waste-water treatment.

European Commission (2020a): COM(2020) 474 final - Critical Raw Materials Resilience: Charting a Path towards greater Security and Sustainability.

European Commission (2020b): COM(2020) 98 final - A new Circular Economy Action Plan For a cleaner and more competitive Europe.

European Commission (2020c): COM(2020) 98 final A new Circular Economy Action Plan For a cleaner and more competitive Europe.

European Commission (2020d): Public consultation (Feedback period 20 Nov. 2020 - 5 March 2021) for the evaluation of sewage sludge use in farming. Available online at https://ec.europa.eu/info/law/better-regulation/have-your-say/initiatives/12328-Evaluation-of-the-Sewage-Sludge-Directive-86-278-EEC-/public-consultation, checked on 6/30/2021.

European Commission (2021): PRICE DASHBOARD No 106 – March 2021 edition.

European Parliament (2015): Directive (EU) 2015/1535 of the European Parliament and of the Council of 9 September 2015 laying down a procedure for the provision of information in the field of technical regulations and of rules on Information Society services (codification). In : Official Journal of the European Union.

EUWID (2020): Remondis und Hamburg Wasser recyceln ab Januar Phosphor. In *EUWID Recycling und Entsorgung*, 12/18/2020. Available online at, https://www.euwid-recycling.de/news/wirtschaft/einzelansicht/Artikel/remondis-und-hamburg-wasser-recyceln-ab-januar-phosphor.html, checked on 6/25/2021.

Ferro, Lorenza; Gorzsás, András; Gentili, Francesco G.; Funk, Christiane (2018): Subarctic microalgal strains treat wastewater and produce biomass at low temperature and short photoperiod. In *Algal Research* 35, pp. 160–167. DOI: 10.1016/j.algal.2018.08.031.

Franchino, Marta; Comino, Elena; Bona, Francesca; Riggio, Vincenzo A. (2013): Growth of three microalgae strains and nutrient removal from an agro-zootechnical digestate. In *Chemosphere* 92 (6), pp. 738–744. DOI: 10.1016/j.chemosphere.2013.04.023.

Franke, Holge (2017): Klärschlammbehandlung mit Phosphor-Rückgewinnung am HKW Mannheim. 3. Kongress Phosphor-Rückgewinnung. Stuttgart - Bad Cannstatt, 11/22/2017. Available online at https://prueck-bw.de/cms/content/media/1.3.3.0_11.Dipl.-Ing.Holger_Franke-Klaerschlamm_mit_Phosphor-Rueckgewinnung.pdf, checked on 8/16/2021.

GERLOFF-ELIAS, ANTJE; SPIJKERMAN, ELLY; SCHUBERT, HENDRIK (2005): Light acclimation of Chlamydomonas acidophila accumulating in the hypolimnion of an acidic lake (pH 2.6). In *Freshwater Biol* 50 (8), pp. 1301–1314. DOI: 10.1111/j.1365-2427.2005.01400.x.

Gross, Martin; Henry, Wesley; Michael, Clayton; Wen, Zhiyou (2013): Development of a rotating algal biofilm growth system for attached microalgae growth with in situ biomass harvest. In *Bioresource Technology* 150, pp. 195–201. DOI: 10.1016/j.biortech.2013.10.016.

Herr, Patrick (2018): Industrial development of Tetraphos®-process, first results with Emscher-Lippe-like SSA (unpublished). 4th working group meeting of the INTERREG VB Nord-West Europe project Phos4You. Rotterdam, 2018.

HGoTech GmbH (2021): Report: P-Supply by EuPhoRe Recycled Phosphate - Winter Term 2020/21. Bonn.

Huijbregts, Mark A. J.; Steinmann, Zoran J. N.; Elshout, Pieter M. F.; Stam, Gea; Verones, Francesca; Vieira, Marisa et al. (2017): ReCiPe2016: a harmonised life cycle impact assessment method at midpoint and endpoint level. In *Int J Life Cycle Assess* 22 (2), pp. 138–147. DOI: 10.1007/s11367-016-1246-y.

Iasimone, F.; Panico, A.; Felice, V. de; Fantasma, F.; Iorizzi, M.; Pirozzi, F. (2018): Effect of light intensity and nutrients supply on microalgae cultivated in urban wastewater: Biomass production, lipids accumulation and settleability characteristics. In *Journal of environmental management* 223, pp. 1078–1085. DOI: 10.1016/j.jenvman.2018.07.024.

IBU-tec advanced materials AG (2016): Entwicklungsversuche zur batchweisen thermischen Behandlung von getrockneten Klärschlämmen im technischen Maßstab im direkt beheizten Drehrohrofen BDO (not published). Bericht. Weimar.

IPCC (2021): Summary for policymakers. In IPCC (Ed.): Climate Change 2021: The Physical Science Basis. Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change. With assistance of V. Masson-Delmotte, P. Zhai, A. Pirani, S.L. Connors, C. Péan, S. Berger et al. in Press: Cambridge University Press.

Irish Water (2020): Annual Environmental Report 2019. Macroom D0126-01. With assistance of Katherine Walshe. Available online at https://www.water.ie/docs/aers/2019/D0126-01_2019_AER.pdf.

Jolliet, Olivier; Saadé-Sbeih, Myriam; Shaked, Shanna; Jolliet, Alexandre; Crettaz, Pierre (2015): Environmental life cycle assessment. Boca Raton: CRC Press. Available online at http://search.ebscohost.com/login.aspx?direct=true&scope=site&db=nlebk&AN=1099097.

Jungbluth, N.; Chudacoff, M.; Dauriat, A.; Dinkel, F.; Doka, G.; Faist Emmenegger, M. et al. (2007): Life Cycle Inventories of Bioenergy. ecoinvent report No. 17. Edited by Swiss Centre for Life Cycle Inventories. Dübendorf, CH.

Kim, Nag-Jong; Lee, Choul-Gyun (2001): A theoretical consideration on oxygen production rate in microalgal cultures. In *Biotechnol. Bioprocess Eng.* 6 (5), pp. 352–358. DOI: 10.1007/BF02933005.

Klein, Daniel; Schmelz, Karl-Georg; Pamuk, Levent; Ploteau, Marie-Edith; Zepke, Frank; Klose, Siegfried (2019): First results of the EuPhoRe pilot plant. In Université de Liège (Ed.): Proceedings. 5th European Conference on Sludge Management Liège. Liège, 6-8 October.

Klose, Ingeborg; Zepke, Frank (2010): Verfahren zur Eliminierung von Schadstoffen aus Klärschlamm und Verfahren zur Herstellung von Phosphaten und phosphathaltigen Verbindungen. Patent no. DE 10 2009 014 884 A1.

Klose, Siegfried (2018): Thermo-chemische Klärschlammbehandlung nach dem EuPhoRe®-Verfahren. In Olaf Holm, Elisabeth Thomé-Kozmiensky, Peter Quicker, Stefan Kopp-Assenmacher (Eds.): Verwertung von Klärschlamm. Neuruppin: Thomé-Kozmiensky Verlag GmbH.

Klose, Siegfried (2021): EuPhoRe-anlage in der Entwicklung to Daniel Klein, 8/3/2021.

Kraus, Fabian (2020): Methodological considerations regarding LCA of P-Recovery processes. 9th working group meeting of the INTERREG VB Nord-West Europe project Phos4You. Kompetenzzentrum Wasser Berlin GmbH. online, 2020.

Krüger, Oliver; Adam, Christian (2014): Monitoring von Klärschlammmonoverbrennungsaschen hinsichtlich ihrer Zusammensetzung zur Ermittlung ihrer Rohstoffrückgewinnungspotentiale und zur Erstellung von Referenzmaterial für die Überwachungsanalytik (TEXTE 49/2014). Available online at https://www.umweltbundesamt.de/en/publikationen/monitoring-von-klaerschlammmonoverbrennungsaschen.

Leleu, David; Pfennig, Andreas (2019): Coalescence Modeling for Design of Technical Equipment. In *Chem. Eng. Technol.* 42 (7), pp. 1404–1413. DOI: 10.1002/ceat.201900037.

Lemley, Daniel A.; Adams, Janine B. (2019): Eutrophication. In : Encyclopedia of Ecology, vol. 25: Elsevier, pp. 86–90.

Liao, Qiang; Li, Lin; Chen, Rong; Zhu, Xun (2014): A novel photobioreactor generating the light/dark cycle to improve microalgae cultivation. In *Bioresource Technology* 161, pp. 186–191. DOI: 10.1016/j.biortech.2014.02.119.

Lin, Li; Yuan, Songhu; Chen, Jing; Xu, Zuqun; Lu, Xiaohua (2009): Removal of ammonia nitrogen in wastewater by microwave radiation. In *Journal of hazardous materials* 161 (2-3), pp. 1063–1068. DOI: 10.1016/j.jhazmat.2008.04.053.

Lösche GmbH (2021): Kurzbericht Mahlversuch_10458 (unpublished). Emscher Klärschlammasche Mahlversuch. Düsseldorf.

Lu, Shuguang; Gibb, Stuart W.; Cochrane, Emma (2007): Effective removal of zinc ions from aqueous solutions using crab carapace biosorbent. In *Journal of hazardous materials* 149 (1), pp. 208–217. DOI: 10.1016/j.jhazmat.2007.03.070.

Luo, Yunlong; Le-Clech, Pierre; Henderson, Rita K. (2017): Simultaneous microalgae cultivation and wastewater treatment in submerged membrane photobioreactors: A review. In *Algal Research* 24 (Part A), pp. 425–437. DOI: 10.1016/j.algal.2016.10.026.

Macintosh, Katrina A.; Chin, Jason; McHugh, Daren; Connolly, Jasmine; O'Flaherty, Vincent; McGrath, John W. et al. (2019): Phosphorus from wastewater: Novel technologies for advanced treatment and re-use (EPA Research Report, 289).

Martínez, M. (2000): Nitrogen and phosphorus removal from urban wastewater by the microalga Scenedesmus obliquus. In *Bioresource Technology* 73 (3), pp. 263–272. DOI: 10.1016/S0960-8524(99)00121-2.

Molina Grima, E.; Belarbi, E.-H; Acién Fernández, F.G; Robles Medina, A.; Chisti, Yusuf (2003): Recovery of microalgal biomass and metabolites: process options and economics. In *Biotechnology Advances* 20 (7-8), pp. 491–515. DOI: 10.1016/S0734-9750(02)00050-2.

Montastruc, L.; Azzaro-Pantel, C.; Biscans, B.; Cabassud, M.; Domenech, S. (2003): A thermochemical approach for calcium phosphate precipitation modeling in a pellet reactor. In *Chemical Engineering Journal* 94 (1), pp. 41–50. DOI: 10.1016/S1385-8947(03)00044-5.

Mooij, T. de (2016): Antenna size reduction in microalgae mass culture. Doctor degree.

Nishikawa, K.; Tominaga, N. (2001): Isolation, growth, ultrastructure, and metal tolerance of the green alga, Chlamydomonas acidophila (Chlorophyta). In *Bioscience, biotechnology, and biochemistry* 65 (12), pp. 2650–2656. DOI: 10.1271/bbb.65.2650.

O´Keeffe, J.; Akunna, J.; Olszewska, J.; Bruce, A.; May, L.; Allan, R. (n.d. [2015]): Practical measures for reducing phosphorus and faecal microbial loads from onsite wastewater treatment system discharges to the environment - A review. Edited by CREW Scotland´s centre of expertise for waters. Aberdeen.

O'Donnell, Ciarán; Egan, Aoife; Harrington, Joe; Barnett, Denise; Forrestal, Patrick; Power, Niamh (2021): An overview on deficit and requirements of the Irish national soil phosphorus balance. In *The Science of the total environment* 785, p. 147251. DOI: 10.1016/j.scitotenv.2021.147251.

Palazzo (2010): What is eutrophication? Causes, effects and control, pp. 1–6.

Pap, Szabolcs; Kirk, Caroline; Bremner, Barbara; Turk Sekulic, Maja; Gibb, Stuart W.; Maletic, Snezana; Taggart, Mark A. (2020a): Synthesis optimisation and characterisation of chitosan-calcite adsorbent from fishery-food waste for phosphorus removal. In *Environ Sci Pollut Res* 27 (9), pp. 9790–9802. DOI: 10.1007/s11356-019-07570-0.

Pap, Szabolcs; Kirk, Caroline; Bremner, Barbara; Turk Sekulic, Maja; Shearer, Lisa; Gibb, Stuart W.; Taggart, Mark A. (2020b): Low-cost chitosan-calcite adsorbent development for potential phosphate removal and recovery from wastewater effluent. In *Water Research* 173, p. 115573. DOI: 10.1016/j.watres.2020.115573.

Pap, Szabolcs; Taggart, Mark A.; Bremner, Barbara; Ploteau, Marie-Edith (2020c): P-rich biomass (Phos4You Information sheet). Available online at https://www.nweurope.eu/media/12161/phos4you_p-rich_biomass_en_nov2020.pdf.

PARFORCE Engineering & Consulting GmbH (2020): Laborversuche, Stoffstrombilanzierung sowie Investitions- und Betriebskostenabschätzung der Phosphorrückgewinnung aus Klärschlammaschen mit der PARFORCE-Technologie im Rahmen des INTERREG VB Projekt Phos4You (unpublished).

PARFORCE Engineering & Consulting GmbH (2021): Vorindustrieller Demonstrationsversuch in der PARFORCE-Pilotanlage inkl. Überarbeitung und Verfeinerung der Stoffstrombilanzierung sowie der wirtschaftlichen Kenngrößen im Rahmen des INTERREG VB NW Phos4You Projektes (unpublished).

Pistocchi, A.; Dorati, C.; Grizzetti, B.; Udias, A.; Vigiak, O.; Zanni, M. (2019): Water quality in Europe. Effects of the urban wastewater treatment directive : a retrospective and scenario analysis of Dir. 91/271/EEC. Luxembourg: Publications Office of the European Union (EUR, 30003).

Ploteau, Marie-Edith (2016): Work plan overview of Pho4You. Project outline of the INTERREG VB NWE application form of Phos4You. Essen.

Ploteau, Marie-Edith; Althoff, Anke; Nafo, Issa; Teichgräber, Burkhard (Eds.) (2021): Final report of the Phos4You partnership: deploying phosphorus recycling from wastewater in North-West Europe. Lippeverband. Essen.

Ploteau, Marie-Edith; Blöhse, Dennis; Bogaczyk, Dirk; Pamuk, Levent; Klein, Daniel; Schmelz, Karl-Georg; Nafo, Issa (2020): Erkenntnisse aus dem EU-Projekt Phos4You zur Phosphorrückgewinnung. In *Korrespondenz Abwasser, Abfall* 67, pp. 502–510. DOI: 10.3242/kae2020.07.001.

Pradel, Marilys; Aissani, Lynda (2019): Environmental impacts of phosphorus recovery from a “product” Life Cycle Assessment perspective: Allocating burdens of wastewater treatment in the production of sludge-based phosphate fertilizers. In *Science of The Total Environment* 656, pp. 55–69. DOI: 10.1016/j.scitotenv.2018.11.356.

Pradel, Marilys; Aissani, Lynda; Villot, Jonathan; Baudez, Jean-Christophe; Laforest, Valérie (2016): From waste to added value product: towards a paradigm shift in life cycle assessment applied to wastewater sludge – a review. In *Journal of Cleaner Production* 131, pp. 60–75. DOI: 10.1016/j.jclepro.2016.05.076.

Rak, A. (2018): Das REMONDIS TetraPhos®-Verfahren. In Olaf Holm, Elisabeth Thomé-Kozmiensky, Peter Quicker, Stefan Kopp-Assenmacher (Eds.): Verwertung von Klärschlamm. Neuruppin: Thomé-Kozmiensky Verlag GmbH, pp. 491–494.

REMONDIS Aqua Industrie GmbH & Co.KG. (2018): Bericht zu Laborversuchen zur Rückgewinnung von Phosphor aus Klärschlammaschen des Verbandsgebietes von Emschergenossenschaft und Lippeverband mit dem REMONDIS TetraPhos®-Verfahren (unpublished).

REMONDIS Aqua Industrie GmbH & Co.KG. (2019): Pilotversuche zur Rückgewinnung von Phosphor aus Klärschlammaschen des Verbandsgebietes von Emschergenossenschaft und Lippeverband mit dem REMONDIS TetraPhos®-Verfahren (unpublished).

Rich, David (2005): The Removal of Total Phosphorus from Natural Waters by Precipitation. A Dissertation Submitted to Northwestern International University in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Environmental Science.

Roskosch, Andrea; Heidecke, Patric; Bannick, Claus-Gerhard; Brandt, Simone; Bernicke, Maja; Dienemann, Claudia et al. (2018): Klärschlammentsorgung in der Bundesrepublik Deutschland. Edited by Umweltbundesamt. Available online at https://www.umweltbundesamt.de/publikationen/klaerschlammentsorgung-in-der-bundesrepublik.

Ruhrverband (2021): Forschungsprojekt AMPHORE zum Phosphorrecycling startet in die Planungsphase. Press release on 23.03. Available online at https://www.ruhrverband.de/presse/pressemitteilungen/detailansicht/news///forschungsprojekt-amphore-zum-phosphorrecycling-startet-in-die-planungsphase/, checked on 6/25/2021.

Ryan, Michael P.; Boyce, Angela; Walsh, Gary (2016): Identification and evaluation of phosphorus recovery technologies in an Irish context. Ireland: Environmental Protection Agency (EPA Research Report, 189).

Schlumberger, Stefan Dr. (2021): Phos4YLife implementation. Phone 15/06/2021 to Dennis Blöhse, 2021.

Schmelz, Karl-Georg; Klein, Daniel; Zepke, Frank (2020): Aufbau, Betrieb und erste Ergebnisse der EuPhoRe-Pilotanlage in Dinslaken. In *wasserwirtschaft wassertechnik* 69. Jahrgang (Nr. 10/2020), pp. 8–12. Available online at https://www.umweltwirtschaft.com/epaper/umw/99/epaper/epaper.pdf.

Schneider, Yvonne (2021): Demonstrationsprojekt AMPHORE. Regionale Strategieentwicklung und Verfahrensauswahl für das Phosphorrecycling aus Klärschlammasche. WebForum Phosphorrückgewinnung, 4. Februar, 2021.

Schweizerischer Bundesrat (4/12/2015): Verordnung über die Vermeidung und die Entsorgung von Abfällen. Abfallverordnung, VVEA. Source: Amtliche Sammlung (AS 2015), pp. 5699–5751. Available online at https://www.admin.ch/opc/de/official-compilation/2015/5699.pdf.

Scottish Environment Protection Agency (SEPA) (2014): Regulatory Method (WAT-RM-37): Regulation of Phosphorous discharges into freshwater lochs, p. 18.

Scottish Environment Protection Agency (SEPA) (2017): Land Use Planning System SEPA Guidance Note 19 (Addendum). Planning advice on waste water drainage.

Shariff, Zaheer; Fraikin, Laurent; Léonard, Angélique; Pfennig, Andreas (2020): Development of solid-liquid-liquid equilibrium speciation and data fitting tool and its application to phosphorus recovery process from sludge. In DECHEMA e.V. (Ed.). Jahrestreffen der ProcessNet-Fachgruppen Fluidverfahrenstechnik, Adsorption und Extraktion. AlpenCongress Berchtesgaden, 26. - 28. Februar. Available online at http://hdl.handle.net/2268/247818.

Shaviv, A.; Mikkelsen, R. L. (1993): Controlled-release fertilizers to increase efficiency of nutrient use and minimize environmental degradation - A review. In *Fertilizer Research* 35 (1-2), pp. 1–12. DOI: 10.1007/BF00750215.

Técnicas Reunidas (2020): PHOS4LIFE™ Technology for Technical Grade Phosphoric Acid Production from Sewage Sludge Ashes (SSA). Proof of Concept Tests (POC) (unpublished).

Tittel, Jörg; Bissinger, Vera; Gaedke, Ursula; Kamjunke, Norbert (2005): Inorganic carbon limitation and mixotrophic growth in Chlamydomonas from an acidic mining lake. In *Protist* 156 (1), pp. 63–75. DOI: 10.1016/j.protis.2004.09.001.

Uduman, Nyomi; Qi, Ying; Danquah, Michael K.; Forde, Gareth M.; Hoadley, Andrew (2010): Dewatering of microalgal cultures: A major bottleneck to algae-based fuels. In *Water science and technology : a journal of the International Association on Water Pollution Research* 2 (1), p. 12701. DOI: 10.1063/1.3294480.

Venkata Subhash, G.; Rohit, M. V.; Devi, M. Prathima; Swamy, Y. V.; Venkata Mohan, S. (2014): Temperature induced stress influence on biodiesel productivity during mixotrophic microalgae cultivation with wastewater. In *Bioresource Technology* 169, pp. 789–793. DOI: 10.1016/j.biortech.2014.07.019.

Veolia Water Technologies (2016): STRUVIA^{TM} – sustainable recycling of phosphorus from wastewater. France, 2016. Available online at https://www.veoliawatertechnologies.com/sites/g/files/dvc2476/files/document/2019/02/3351%2C150354_Mkt_Mun_Brochure_STRUVIA_EN_.pdf, checked on 6/29/2021.

Verma, Srishti; Daverey, Achlesh; Sharma, Archana (2017): Slow sand filtration for water and wastewater treatment – a review. In *Environmental Technology Reviews* 6 (1), pp. 47–58. DOI: 10.1080/21622515.2016.1278278.

Wernet, Gregor; Bauer, Christian; Steubing, Bernhard; Reinhard, Jürgen; Moreno-Ruiz, Emilia; Weidema, Bo (2016): The ecoinvent database version 3 (part I): overview and methodology. In *Int J Life Cycle Assess* 21 (9), pp. 1218–1230. DOI: 10.1007/s11367-016-1087-8.

Westfälisches Umwelt Zentrum (2020): Versuche zur Ausfällung von gelösten Phosphorverbindungen aus kommunalem Abwasser unter Einsatz von zwei verschiedenen Fälmitteln (unpublished). With assistance of Volker Pick.

Zheng, Yulin; Wang, Bing; Wester, Anne Elise; Chen, Jianjun; He, Feng; Chen, Hao; Gao, Bin (2019): Reclaiming phosphorus from secondary treated municipal wastewater with engineered biochar. In *Chemical Engineering Journal* 362, pp. 460–468. DOI: 10.1016/j.cej.2019.01.036.

DOI: 10.17185/duepublico/74788
URN: urn:nbn:de:hbz:464-20210920-094346-4

The project Phos4You is co-funded from the European Regional Development Fund within the INTERREG North-West Europe VB Programm.

EGLV Lippeverband

Interreg North-West Europe Phos4You

www.nweurope.eu/phos4you