MODELING AND OPTIMIZATION OF SYSTEMS FOR NUTRIENT RECOVERY FROM LIVESTOCK WASTE

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Informa:

Que la memoria titulada: "Modeling and optimization of systems for nutrient recovery from livestock waste", que para optar al Grado de Doctor en Ciencia y Tecnología Química con Mención Internacional presenta **D. Edgar Martín Hernández**, ha sido realizada bajo nuestra dirección dentro del Programa de Doctorado Ciencia y Tecnología Químicas (RD 99/2011) de la Universidad de Salamanca, y que considerando que constituye un trabajo de tesis.

Autoriza:

Su presentación ante la Escuela de Doctorado de la Universidad de Salamanca, mediante el formato de compendio de publicaciones.

Y para que conste a los efectos oportunos, firmo la presente en Salamanca, a 01 de diciembre de 2021.

Fdo: Mariano Martín Martín

A mi familia, y a todos los que por mi vida pasaron.

Non exiguum temporis habemus, sed multum perdimus.
Satis longa vita et in maximarum rerum consummationem
large data est, si tota bene collocaretur;
sed ubi per luxum ac neglegentiam diffluit,
ubi nulli bonae rei impenditur,
ultima demum necessitate cogente quam ire non
intelleximus transisse sentimus.

— Lucius Annaeus Seneca, De brevitate vitae.

No tenemos un tiempo escaso, sino que perdemos mucho.
La vida es lo bastante larga para realizar las mayores empresas,
pero si se desparrama en la ostentación y la dejadez,
donde no se gasta en nada bueno, cuando al final
nos acosa el inevitable trance final, nos damos cuenta
de que ha pasado una vida que no supimos que estaba pasando.

— Lucius Annaeus Seneca, De la brevedad de la vida.

ACKNOWLEDGMENTS

Complete

ABSTRACT

To be completed.

RESUMEN

Completar.

PUBLICATIONS

This thesis is presented as a compendium of publications, where each of the chapters corresponds to a formal manuscript published in a scientific journal, or currently under review, and book chapters. The relation of manuscripts published or under review, and book chapters that comprise this dissertation is detailed below:

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INTRODUCTION

1.1 RATIONALE: OVERVIEW OF THE NUTRIENT POLLUTION CHALLENGE

Human population is experiencing a continuous growth since the end of the Black Death in the XIV century (**biraben1980essay**), which is at 7.8 billion as of 2020, and it is estimated to be at 9.7 billion and 10.9 billion by 2050 and 2100 respectively (**UNPopulationProspects**). Population growth demands increasing amounts of food, which in turn requires an efficient food production system to ensure global food security. In this context, the development of different technical advancements has been a key factor to increase the productivity of the food production system. Notably, crucial developments were achieved in the late modern period[1], including the commercial production of phosphate in 1847 (**Samreen2019**), the development of the Haber-Bosch process for the production of synthetic nitrogen-based fertilizers in 1913 (**smil1999detonator**), and the mechanization of agriculture and the development of the modern intensive farming in the XX century (**constable2003century**; **nierenberg2005happier**).

Despite these advancements have increased the productivity of agriculture and farming industries, multiple environmental impacts associated with them emerges, including water scarcity, greenhouse gases emissions, nutrient pollution of waterbodies, and soil degradation, among others. These threats must be carefully addressed in order to avoid the depletion of natural resources and reach a sustainable food production system.

Focusing on the impacts derived from agriculture and farming on the nutrient cycles, it can be observed that the natural cycles of phosphorus and nitrogen have been altered by these activities (**Bouwman2009**). Large amounts of nutrients are released into the environment in the form of synthetic fertilizers and livestock manure. Nitrogen and phosphorus are accumulated in soils, creating a nutrient legacy that is further transported to waterbodies by runoff. This process results in the eutrophication of waterbodies, which can lead algal bloom episodes. Algal blooms are events resulting from the rapid increase of algae in a water system which can

1 The terminology used in this dissertation for the periodization of human history follows the English-language historiographical approach. It should be noted that the late modern period is referred to as the contemporary period in the European historiographical approaches.

be promoted by an excess of nutrients in water. These episodes alter the normal functioning of aquatic ecosystems, since they cause hypoxia as a consequence of the aerobic degradation of algal biomass by bacteria. Moreover, some species of algae that cause algal blooms can releases toxins into the water systems. The main flows of nutrient releases into the environment by anthropogenic activities is shown in Figure 1.1.

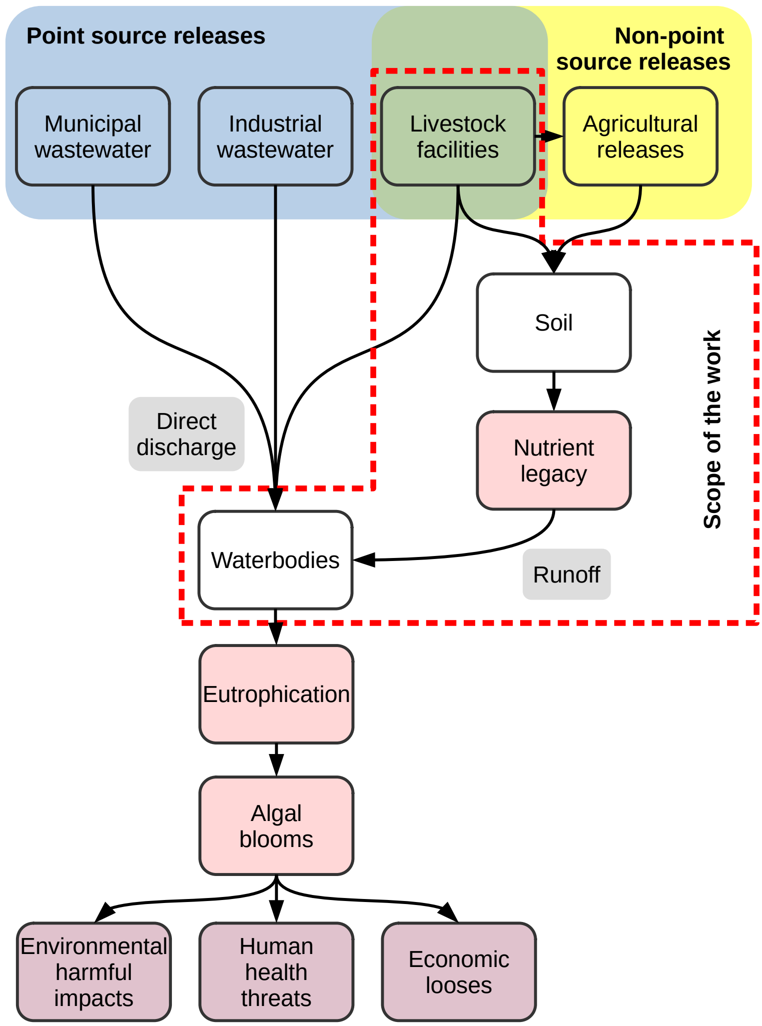

Figure 1.1: Main flows of nutrients released by anthropogenic activities.

In addition to the environmental problems, the use of nutrients for food production also raises geopolitical concerns since phosphorus is one to the most sensitive elements to depletion. Phosphorus is a non-renewable material whose reserves are expeted to be depleted in the next 50 to 100 years. Moreover, no substitute material is currently known (**cordell2009story**). Conversely, synthetic nitrogen can be produced using the atmospheric N_2

as raw material through the Haber-Bosh process. However, nowadays this process relies on non-renewable energy sources, and therefore the production of synthetic nitrogen–based fertilizers is dependent on non-renewable resources as well.

Considering the two challenges described, i.e., nutrient pollution of waterbodies as a consequence of agricultural and farming activities, and the current dependency on non-renewable resources for the production of synthetic fertilizers, nutrient recovery and recycling is not only a desirable but also a necessary approach to develop a sustainable agricultural paradigm and ensure the global food security.

Attending to the nutrient releases from intensive livestock farming facilities, known as concentrated animal feeding operations (CAFOs)[2], several manure management techniques are currently used. The land application of manure is a common technique that allows the recycling of nutrients as fertilizers for crops (**Kellog2010**). However, the increase of intensive livestock farming generates vast amounts of waste generated by CAFOs, e.g., each adult cow generates between 28 and 39 kg of manure per day, and each adult pig generates around 11.5 kg of manure per day (**USDAHandbook**). Manure processing is commonly based on the separation of liquid and solid phases. The liquid phase can be treated in anaerobic and/or aerobic lagoons for organic matter and pathogens removal, as well as odor control (**tilley2014compendium**). The obtained liquid effluent can be used for irrigation and nutrient supplementation of crops. The solid phase can be composted for the degradation of organic matter and pathogens removal, resulting in a solid material called compost with a larger amount of nitrogen and phosphorus available for plants, which is result of the mineralization of nutrients previously contained in organic compounds. Since compost is also a good source of organic matter for crops, it is a valuable material suitable for sale (**tilley2014compendium**). However, both materials, the liquid effluent obtained from the lagoons and compost, are too bulky to be economically transported to nutrient deficient locations (**burns2002phosphorus**). As a result, livestock waste is usually spread in the surroundings of livestock facilities, at a detrimental cost of environment. This result in the gradual build-up of nutrients in soils, which might lead the harmful environmental impacts previously described.

A promising alternative for abating nutrient releases and reducing the environmental footprint of livestock industry is the implementation of processes for the recovery of phosphorus and nitrogen at CAFOs. At the

2 CAFO is a regulatory term defined by the U.S. Environmental Protection Agency for large facilities where animals are kept and raised in confined situations (**animal_unit_definition**). This term is used in this dissertation to denote the intensive livestock farming facilities studied.

time, that valuable nutrient-rich materials are obtained for the redistribution of phosphorus and nitrogen to nutrient-deficient areas. There exist a number of processes for nutrient recovery from livestock waste, which can be differentiated into those technologies oriented to phosphorus recovery, including struvite precipitation, calcium-based precipitates production, coagulation-flocculation, electrochemical processes, and systems based on solid-liquid separation; and processes focused on nitrogen recovery, such as stripping, membrane separation, waste drying coupled with ammonia scrubbing, and solid-liquid separation processes. We note that anaerobic digestion is an additional process that can be integrated for manure treatment if the generation of biomethane is pursued, and for increasing the amount of recoverable nutrients through the partial mineralization of nutrients contained in organic compounds. It must be noted that only phosphorus and nitrogen in inorganic compounds can be taken by plants, and therefore the recovery of inorganic nutrients will be the target of the processes studied in this thesis.

The multiple processes for the recovery of phosphorus and nitrogen from livestock waste differ in aspects such as recovery efficiency, processing capacity, capital and operating costs, and products obtained. Therefore, a detailed analysis of each CAFO must be performed in order to select the optimal nutrient recovery system attending to type factors such as the type and amount of waste to be processed, the environmental vulnerability to eutrophication of each region, the current or potential installation of anaerobic digestion systems, etc. Additionally, in the decision-making process these factors have to be prioritized, i.e., sorted by relevance, to select the most suitable nutrient recovery system for each particular facility. As example, more economical processes for nutrient recovery, whose recovery efficiencies are typically lower, could be installed in regions with a low risk of eutrophication. Conversely, regions at severe eutrophication risk require highly efficient nutrient recovery systems that may incur in larger investment and operating expenses. In order to perform a systematic evaluation of CAFOs and their context, we introduce a multi-criteria decision analysis (MCDA) framework integrating geospatial environmental data on eutrophication risk at the subbasin level and techno-economic information of the studied processes.

Attending to the regulatory aspect, nowadays most of the efforts for abating of nutrient releases into the environment and mitigating the eutrophication of waterbodies are focused on the limitation of fertilizer application in croplands. The application of fertilizer and manure for nitrogen supplementation in the European Union (EU) is currently regulated by the Nitrates Directive (91/676/EEC) (**GRIZZETTI2021102281**). Regarding the limitations for phosphorus application, these are defined at national level. Several European countries have implemented phosphorus application standards based on the different crops and materials used as fertilizers, being generally more restrictive in Northwestern Europe (**amery2014agricultural**).

In sum, it can be observed that nutrient application is limited either in the form of synthetic fertilizers or manure application. However, at present there is a lack of regulation regarding livestock waste treatment (**Piot_Lepetit2012**). In this regard, new efforts to promote the production and adoption of bio-fertilizers obtained from organic waste are being performed through the development of the "Integrated Nutrient Management Plan" (INMAP), which is part of the EU Farm-to-Fork strategy and part of the Circular Economy Action Plan. INMAP should propose actions to promote the recovery and recycling of nutrients, as well as the development of markets for recovered nutrients (**ESSP2021**; **CircularEconomyActionPlan**). In this regard, a new regulation for fertilizer products has been released in 2019 (EU 2019/1009), moving struvite and other biofertilizers from the category of waste to fertilizers, establishing a regulatory framework for their use and trade.

In the United States, CAFOs are regulated under the Clean Water Act as point source waste discharges. This regulation sets the need of permits for discharging pollutants to water, which are called National Pollutant Discharge Elimination System (NPDES) permits, including nitrogen and phosphorus releases. These permits must include the necessary provisions for avoiding the harmful effects of the discharges on water and human health (**NPDE_basics**). The development and implementation of a Nutrient Management Plan (NMP) is a required element to obtain an NPDES permit. This document must identify the management practices to be implemented at each CAFO to protect natural resources from nutrient pollution. Land spreading of manure can also be regulated by the NPDES permits, establishing soil nutrient concentration limits and the yearly schedule for manure application. However, no specific methods or processes for waste treatment are defined under federal regulation (**NPDESforCAFO**). Regarding the use of the recovered nutrients, products obtained from nutrient recovery processes could be classified as waste ny the Clean Water Act, preventing the application of these materials on croplands (**NACWA503**). However, the U.S. Environmental Protection Agency (US EPA) determined that, although these products could not be directly applied to land under the current regulation, they can be sold as a commodity to be outside of the Clean Water Act restrictions coverage (**CNP503**). Moreover, US EPA acknowledges that highly refined and primarily inorganic products (such as struvite) could be outside of the scope of these restrictions (**CNP503**). Nevertheless, further regulation is needed for defining the products obtained from nutrient recovery processes and to clearly state the conditions for their use as fertilizers on croplands.

Considering the previously described aspects, we note that the regulation of the products obtained from nutrient recovery systems is not totally developed yet either in the European Union and the United States, although important efforts are being performed in order to set a comprehensive regulatory framework for the recycling of phosphorus and nitrogen. Furthermore, no regulation regarding the implementation of nutrient recovery processes has been developed However, both regions have developed previous programs to study and promote the implementation of other technologies for the treatment of livestock and other organic waste. Particularly, the deployment of anaerobic digestion systems have received a considerable support from governmental agencies, resulting in programs such as AgSTAR in the US (**AgSTARProgram**), and BiogasAction (**BiogasAction**) and BIOGAS[3] (**BIOGAS3PROJECT**) in Europe, among many others. These programs could be a guideline for the development of nutrient recovery plans at CAFOs. In this regard, we have studied the impact of the implementation of nutrient recovery systems in the economy of CAFOs, either considering the deployment of standalone nutrient recovery processes, or integrated systems combining nutrient recovery with anaerobic digestion for the production of electricity and biomethane. Moreover, incentive policies have been analyzed to minimize the negative impact of nutrient recovery on CAFOs economy using the Great Lakes area as case study. In addition, the fair distribution of monetary resources when limited budget is available has been studied using the Nash allocation scheme.

An overview of the main topics studied in this thesis can be observed in Figure 1.2. This work pretends to analyze strategies for promoting effective nutrient recycling addressing studies on the technical, environmental and economic dimensions involved, pursuing the development of sustainable food production paradigm.

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1.2 APPROACHES FOR PROCESSES MODELING

Process modeling, defined as the mathematical modeling and simulation of systems, falls under the scope of the Process System Engineering (PSE) discipline. These systems include physical, chemical, and/or biological operations. Process modeling forms the foundation for other activities involved in the scope of PSE, including process design, optimal

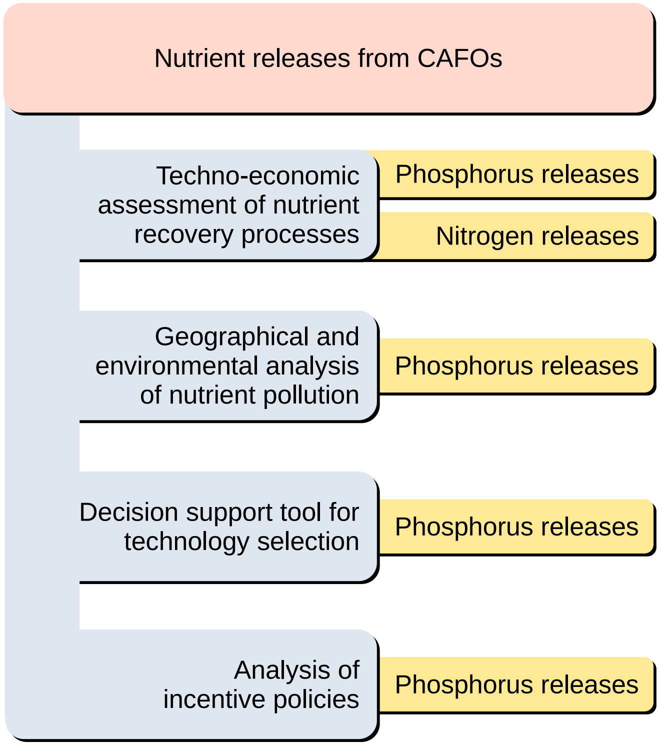

Figure 1.2: Main topics covered in this work.

scheduling and planning of the systems operations, and process control (**STEPHANOPOULOS20114272**).

Different modeling techniques have been developed to mathematically describe and represent systems from different domains, including but not limited to the chemical, biochemical, agrochemical, food, and pharmaceutical domains of engineering (**PISTIKOPOULOS2021107252**). An overview of the main modeling techniques is shown in the next sections based on the classification proposed by **MARTIN201216**.

1.2.1 *Short-cut methods*

These type models are the most basic approach to process modeling. They are based on mass, energy, and momentum balances, and can be embedded in other models, such as supply chain models.

1.2.2 *Rules of thumb*

This approach is based on industrial operational data. It provides typical ranges for operating and design values, reflecting the actual parameters of the systems modeled. However, the use of these models is constrained by the availability of data. Compendiums of rules of thumb for different systems can be found in **couper2005chemical**; **hall2012rules**; **sadhukhan2014biorefineries**.

1.2.3 *Dimensionless analysis*

This methodology is based on dimensionless groups that describe the performance of a particular system. These models are able to capture the physical meaning of the modeled processes, and they are specially useful to capture scale-up and scale-down issues (**szirtes2007applied**).

1.2.4 *Mechanistic models*

This approach relies on first principles for systems modeling, as short-cut models. However, mechanistic models rely in more detailed first principles such as the underlying chemistry, physics or biology that governs the behavior of a particular system. Chemical (**loeppert1995chemical**) and phase (**brignole2013phase**) equilibrium models, kinetic models (**buzzi2009kinetic**), population balances (**ramkrishna2000population**), and computer fluid dynamics (CFD) (**anderson1995computational**) fall under this category.

1.2.5 *Surrogate models*

These models aim at developed simplified models from data obtained from rigorous mechanistic models. This approach is widely used for embedding system models into other applications such as process control or supply chain design. Surrogate models building has been systematized into four steps, i.e., design of experiments (DOE), running the rigorous models at the sampling points designated by the DOE, construction of the surrogate model, and validation of the model obtained (**queipo2005surrogate**).

Polynomial regression models, in which the relationship between the variables is expressed using a polynomial function, are one of the most basic types of surrogate models. In the case of polynomial regression models involving multiple variables, the optimal variables to be addressed within the pool of variables considered can be determined by using machine learning-based tools such as ALAMO (**wilson2017alamo**), ensuring an optimal trade-off between model accuracy and complexity. Other types of surrogate models are Kriging models, which estimate the relationship between variables as a sum of a linear model and a a stochastic Gaussian function representing the fluctuations of data (**quirante2015rigorous**), and artificial neural networks (ANN), which are based on generating an input signal as the summation of all the weighted inputs, which is through nodes containing a transfer function. Nodes are connected by edges with assigned weights that adjust the signals transmitted between nodes. Nodes are structured in layers, in a way that nodes receive signals from nodes of the preceding layer, and if the output of the node is above a threshold value defined by the transfer function, sends the output signal to the next layer (**himmelblau2000applications**).

1.2.6 *Experimental correlations*

As the surrogate models, experimental correlations are models built using data of the systems represented, but converserly to those one, experimental correlations are built using data from experimental results. Similarly to the rules of thumb, the accuracy of these models is limited by the availability of data, and they are only applicable to the range of operating conditions of the data used for constructing the model.

1.3 APPROACHES FOR DECISION-SUPPORT SYSTEMS

Decision-making activities require to analyze multiple relevant criteria for each course of action. Since criteria often conflict each other, each decision-making process requires the balancing of criteria, prioritizing some criteria over other through the use of some criteria weighting scheme. This procedure requires managing a vast amount of information of conflicting nature, leading to a complex decision-making process. Therefore, different approaches generally called multiple-criteria decision analysis (MCDA) have been developed to explicitly structure and solve decision problems. MDCA aim is to integrate criteria assessment with value judgment to analyze and compare the different available alternatives, identifying the best solution for the specific decision-making context studied. However, it must be highlighted that a certain grade of subjectivity might exist is several steps of MCDA, such as the choice of the set of criteria considered relevant for a particular problem. Therefore, the solution proposed by any MCDA approach must be analyzed considering the assumptions made for building the problem. In sum, MCDA seeks to structure problems with multiple conflicting criteria, and providing justifiable and explainable solutions to guide decision-makers facing such problems. The solution of a multiple-criteria decision-making problem can be defined as a unique solution representing the most suitable alternative from the set of potential alternatives, or as a subset of satisfactory alternatives (**belton2002multiple**).

An MCDA problem can be articulated in different stages, starting with the problem definition and structuring. At this stage, the goals, constraints, and stakeholders comprising the problem are defined, as well as the different solution alternatives. Based on this information, a model can be built for the assessment and comparison of alternatives. This stage includes the definition of the relevant criteria used for alternatives comparison, their relative priority, and the system for criteria evaluation. Finally, the information retrieved by the model can be used for making informed decisions.

Multi-criteria decision-making problems can be classified into Multi-Attribute Decision Analysis (MADA), which are discrete choice problems where the number of alternatives is finite, and Multi-Objective Decision Analysis (MODA), that are mathematical programming problems that consider infinite number of alternatives, as shown in Figure 1.3. However, we note that mathematical programming techniques are not limited to formulating and solving problems with infinite alternatives, but they can also be used for dealing with discrete decision-making problems (**giove2009decision**).

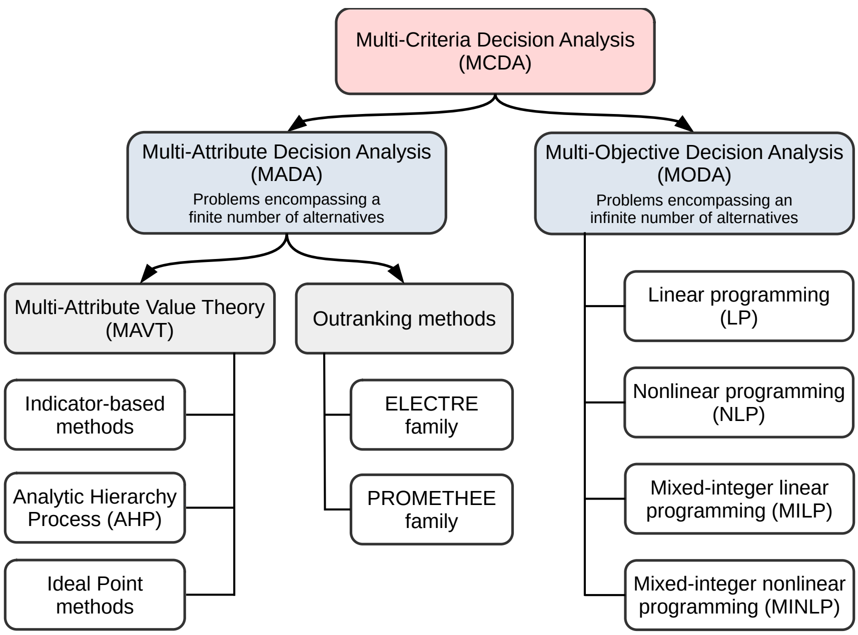

Figure 1.3: Classification of MCDA methods.

1.3.1 *Multi-Attribute Decision Analysis (MADA)*

In the case of problems consisting of a finite number of alternatives, the suitability of each alternative to the problem given can be measured through its performance according to the multiple criteria considered. A large number of MCDA approaches have been (and are currently being) developed for discrete choice problems, including methods based on value functions (Multi-Attribute Value Theory methods, MAVT) and outranking methods.

1.3.1.1 *Multi-Attribute Value Theory (MAVT)*

INDICATOR-BASED METHODS Multi-Attribute Value Theory (MAVT) approaches are based on an indicator-based methodology for alternatives comparison. The relevant criteria considered in the decision-making process are normalized to a common scale to allow criteria comparison using an utility or value function. A number of utility functions have been proposed in the literature, including standardization, min-max, and target utility functions (**HandbookCompositeIndicators**). The normalized criteria are weighted and aggregated to build a composite index, prioritizing some criteria over others. Different aggregation schemes have been proposed, providing different degrees of compensability between indicators, i.e. a deficit in one criteria can be fully, partially, or not compensated by a surplus in other criteria (**MarcoCinelli2020**). Additive weighting aggregation is a full compensatory method, while geometric and harmonic aggregation methods are partial compensation schemes. Other aggregation schemes include geometric averaging, which is a non-compensatory method, and the Choquet integral (**marichal2000determination**). The composite index obtained is a single numerical value that can be used to score and rank the proposed alternatives based on their suitability to the criteria considered.

A major source of uncertainty in indicator-based methods is the value of criteria weights. This issue can be addressed using the stochastic multi-criteria acceptability analysis (SMAA) method. SMAA is a sensitivity analysis method that address the uncertainty of criteria weights value exploring the feasible space of weights through the Monte Carlo method. Further, details about the SMAA approach can be found in **tervonen_implementing_2007**.

In this thesis, and indicator-based methodology has been used to assess and select phosphorus recovery technologies based on technical, environmental, and economic criteria combined in a composite index, as it is shown in Chapter .

ANALYTIC HIERARCHY PROCESS (AHP) Analytic Hierarchy Process (AHP) decomposes the decision problem into multiple simpler sub-problems. These sub-problems are hierarchized and independently analyzed. The sub-problems are solved through the pairwise comparison of alternatives, obtaining numerical indexes that can be used to compare their performance. Finally a numerical weight (priority) is assigned to each element of the hierarchy, and they are used for aggregating the indexes obtained by each alternative at each element of the hierarchy in a final numerical value that can be used to score the overall performance of each alternative accordingly to the set of criteria considered (**saaty2000fundamentals**).

IDEAL POINT METHODS Ideal Point methods set an optimal solution, that represent a utopia point where all criteria values are optimal. The performance of each alternative is evaluated through a composite index, that can be constructed using the MAVT approach. The alternatives are ranked based on their relative distance relative to the optimal solution. One of the most common Ideal Point methods is TOPSIS (**hwang1995multi**).

1.3.1.2 *Outranking methods*

Outranking methods are based on the pairwise comparison of the alternatives for each criterion considered, determining the preferred alternative for each of the criteria. Preference information about all criteria is aggregated to establish evidence for selecting one alternative over another. These methods indicate the dominance of one alternative over another, but they do not quantify the performance gap between the alternatives compared (**giove2009decision**). Some of the most popular outranking methods are ELECTRE I (**roy1968classement**), II (**roy1973methode**), and III (**roy1978electre**), and PROMETHEE (**vincke1985preference**).

1.3.1.3 *Multi-Objective Decision Analysis (MODA)*

Problems consisting of an infinite number of solutions require multi-objective mathematical programming (optimization) techniques to be solve. These problems are subjected to a number of equality and/or inequality constraints restricting the solutions that are feasible. The multiple conflicting criteria are combined in an objective function. This objective function represents the improving level of the criteria, and it will be minimized or maximized for selecting the best solution that represents the optimal trade-off between the different conflicting criteria (**giove2009decision**). In this thesis, this technique has been employed for determining the operating conditions of processes for the recovery of nutrient, energy and biomethane from livestock waste, as it is shown in Chapters **??** and **??**. Other approach for solving multi-objective mathematical programming problems is to set a priori targets for different criteria, or combinations of criteria, that are considered satisfactory, obtaining the problem solution by minimizing the deviations from these goals. Mathematical programming problems can be also classified according to the use of linear or nonlinear equations, and continuous and/or discrete variables (**giove2009decision**).

LINEAR PROGRAMMING (LP) Linear programming (LP) refers to those mathematical programming problems based on linear equations and continuous variables. A linear programming problem can be expressed as shown in Eq. 1.1, where x is a vector of dimension n, A is a mxn matrix, c is the n dimension vector of cost coefficients, and the right-hand side b is a vector of dimension m (**grossmann2021advanced**).

$$\begin{aligned} \min \quad & Z = c^T x \\ \text{s.t.} \quad & Ax \leq b \\ & x \geq 0 \end{aligned} \tag{1.1}$$

The two most widely used methods to solve LP problems are the Simplex algorithm (**murty1983linear**) and interior-point methods (**POTRA2000281**). The Simplex method is more efficient for solving problems with thousands of variables and constraints, while interior-point is more efficient on very large scale and sparse problems (**grossmann2021advanced**). These methods are implemented in solvers such as CPLEX (**cplex2009v12**), Gurobi (**gurobi**), or XPRESS (**xpress**).

NONLINEAR PROGRAMMING (NLP) Nonlinear programming (NLP) refers to those mathematical programming problems containing nonlinear equations, either in the constrains or in the objective function, and continuous variables. A nonlinear programming problem can be expressed as shown in Eq. 1.2, where x is an n dimension vector, $f(x)$ is the objective function of the problem, $h(x)$ is the set of equality constraints and $g(x)$ is the set of inequality constraints (**floudas1995nonlinear**).

$$\begin{aligned} \min \quad & f(x) \\ \text{s.t.} \quad & h(x) = 0 \\ & g(x) \leq 0 \\ & x \in X \subseteq \Re^n \end{aligned} \tag{1.2}$$

Some of the most common algorithms to solve NLP problems are successive quadratic programming (SQP), reduced gradient algorithms, and interior point methods.

SQP algorithms are based on the solution of quadratic programming subproblems. Each subproblem optimizes a quadratic model of the objective function subject to linearized constraints. In each of the iterations a search direction is determined reducing some merit function to ensure problem convergence (**gill2005snopt**). SNOPT is a solver based on this method (**gill2005snopt**).

Reduced gradient methods consider a linear approximation of the constraints and eliminate variables to reduce the dimension of the problem. The resulting problem is solved by applying the Newton's method. In each of the iterations, the reduced gradient is calculated, the search direction is determined, and finally a line search is performed minimizing the objective function. MINOS (**murtagh1983minos**) or CONOPT (**drud1985conopt**) are solvers based on this algorithm.

Interior point methods reformulate the original NLP problem by means of slack variables to replace the inequalities by equalities and the log-barrier function to handle the non-negativity of the x variables. The new problem is solve applying the Newton's method. IPOPT **wachter2006implementation** and KNITRO (**waltz2004knitro**) are solvers based on this approach

MIXED-INTEGER LINEAR PROGRAMMING (MILP) Mixed-integer linear programming (MILP) refers to those mathematical programming problems based on linear equations and containing discrete variables. A mixed-integer linear programming problem can be expressed as shown in Eq. 1.3,where x are continuous variables and y are discrete variables. Typically, discrete variables are binary variables (**grossmann2021advanced**).

$$\begin{aligned} \min \quad & Z = a^T x + b^T y \\ \text{s.t.} \quad & Ax + By \leq d && (1.3) \\ & x \geq 0 && (1.4) \\ & y \in \{0,1\}^m \end{aligned}$$

A number of methods have been proposed to solve MILP problems, including cutting planes, Benders decomposition, branch and bound search, and branch and cut methods.

Cutting planes consist of a sequence of LP problems in which different cutting planes are generated to cut-off the solution of the relaxed LP. They reduce the feasible region of the linear relaxation of the original problem excluding those solutions that are feasible in the linear relaxation but not in the original MILP problem.

Benders decomposition is based on the generation of a lower and an upper bound of the solution of the MILP problem in each iteration. The upper bound is calculated from the primal problem, which correspond with the original problem where the binary variables have been fixed. Conversely, the lower bound is determined through a master problem, which is a LP problem derived from the original problem by means of the duality theory. Branch and bound method structure the problem in form of a binary tree that includes all possible combinations of binary variables. The tree is explored by solving the relaxed versions of the original problem. If the relaxation does not result in an integer solution (0 or 1), it is necessary to go deeper into the solution tree to explore further combinations of the binary variables. If the result obtained is an integer, the next step is to return to the previous subproblem to explore the alternative branch. However, diverse procedures have been developed to discard certain branches, avoiding the need of exploring the whole tree and reducing the problem (**floudas1995nonlinear**).

Branch and cut methods combine branch and bound methods with cutting planes targeting a tighter lower bound. In the different nodes, the relaxed problem is solved. If the solution is not integer, the relaxing problem is solved by adding cutting planes in order to strengthen the lower bound (**grossmann2021advanced**). Gurobi (**gurobi**) and CPLEX (**cplex2009v12**) are solvers based on this approach.

MIXED-INTEGER NONLINEAR PROGRAMMING (MINLP) Mixed-integer nonlinear programming (MINLP) refers to those mathematical programming problems containing nonlinear equations and discrete variables, typically, binary variables. A mixed-integer nonlinear programming problem can be expressed as shown in Eq 1.5, where x represents a vector of continuous variables, y is the vector of binary variables, $h(x,y)$ and $g(x,y)$ denote the equality and inequality constraints respectively. $f(x)$ represents the objective function (**grossmann2021advanced**).

$$\begin{aligned} \min \quad & f(x,y) \\ \text{s.t.} \quad & h(x,y) = 0 \\ & g(x,y) \leq 0 \\ & x \in X \subseteq \Re^n \\ & y \in \{0,1\}^m \end{aligned} \tag{1.5}$$

Some algorithms for solving MINLP problems are the generalized Benders decomposition, outer approximation, and generalized cross decomposition.

Generalized Benders decomposition (GBD) is based on the generation of a lower and an upper bound of the solution of the MINLP problem in each iteration. Similarly to the Benders decomposition, the upper bound is calculated from the primal problem, which correspond with the original problem where the binary variables have been fixed. The lower bound is determined through a master problem, which is a LP problem derivated from the original problem by means of the duality theory. In addition, the master problem provides information about the binary variables to be fixed in the next iteration (**floudas1995nonlinear**).

Outer approximation (OA) provides a lower and an upper bound in each iteration. As the previous case, the upper bound is calculated from the primal problem. The lower bound is calculate from a master problem obtained based on an outer approximation, i.e., the nonlinear objective function and the constraints are linearized around the primal solution. Additionally, the master problem provides information about the binary variables to be fixed in the next iteration.

Generalized cross decomposition (GCD) is based on the generation of a primal problem that provides an upper bound of the solution and also the Lagrange multipliers for the dual subproblem. The dual problem is used to determine the lower bound of the problem, and provides a vector of binary variables to be fixed in the primal problem. The solution of the primal and dual problems go through convergence tests. If any of these test fails, a master problem is solved. This approach seeks to minimize the number of master problems to be solved since the computational requirements of the this problem are higher. This procedure is repeated at each iteration of the algorithm (**floudas1995nonlinear**).

1.4 APPROACHES FOR GEOSPATIAL ENVIRONMENTAL ASSESSMENT

The development of mitigation measures to reduce the environmental footprint of anthropogenic activities requires the previous understanding and quantification of the environmental impacts associated to each sector. This process, called environmental impact assessment (EIA), involves the analysis of multi-disciplinary information, including environmental, physical, geological, ecological, economic, and social data (**gharehbaghi2018gis**). Since EIA aims to evaluate the environmental impact of an activity on a particular geographical location, all these data have a common geographic component, becoming geospatial data.

Geospatial data can be managed and analyzed through specific systems denoted as geographic information system (GIS). GIS is a key tool for EIA that uses the geographic component of geospatial data as an integrative framework that provides the ability to analyze and map the descriptive information of the locations studied. The geographic component of data is the key element of GIS systems, since the spatial (or spatio-temporal) location is used as a key to relate other descriptive information. From the perspective of EIA, this information can be analyzed, interpreted, and mapped in order to determine the vulnerability level to a particular environmental threat at each location, find relationships between human activities and environmental damages, measure the performance of mitigation and remediation processes, etc.

As a result, the combination of GIS, EIA, and methods for the analysis of multi-dimensional information, such as MCDA, provides tools for the development of strategies to promote the transition to a sustainable paradigm for human growth. In this regard, the development of a sustainable, reliable, and resilient water, energy and food nexus is a major issue for food security and environmental protection.

1.5 THESIS OUTLINE

This dissertation is structured in three parts. Part I is devoted to the study of phosphorus management and recovery, Part II addresses a techno-economic assessment of the technologies for nitrogen recovery, and Part III conducts a techno-economic analysis for determining the optimal biomethane production process in order to integrate biogas production and nutrient recovery processes.

1.5.1 *Part I - Phosphorus management and recovery*

CHAPTER **??** - TECHNOLOGIES FOR PHOSPHORUS RECOVERY. This chapter performs a review of the main processes for phosphorus recovery from livestock waste, identifying the most promising processes to be deployed at CAFOs using a mixed-integer nonlinear programming model.

CHAPTER 3 - ASSESSMENT OF PHOSPHORUS RECOVERY THROUGH STRUVITE PRECIPITATION. This chapter studies the mitigation of phosphorus releases through the deployment of struvite precipitation systems in the watersheds of the contiguous Unites States. Specific surrogate models to predict the production of struvite and calcium precipitates from cattle leachate were developed based on a detailed thermodynamic model.

In addition, the variability in the organic waste composition is captured through a probability framework based on the Monte Carlo method.

CHAPTER 4 - GEOSPATIAL ENVIRONMENTAL AND TECHNO-ECONOMIC FRAMEWORK FOR SUSTAINABLE PHOSPHORUS MANAGEMENT AT LIVESTOCK FACILITIES. This chapter presents a decision support framework, COW2NUTRIENT (Cattle Organic Waste to NUTRIent and ENergy Technologies), for the assessment and selection of phosphorus recovery technologies at CAFOs based on environmental information on nutrient pollution and techno-economic criteria. This framework combines eutrophication risk data at subbasin level and the techno-economic assessment of six state-of-the-art phosphorus recovery processes in a multi-criteria decision analysis (MCDA) model. We aimed to provide a useful framework for the selection of the most suitable P recovery system for each particular CAFO, and for designing and evaluating effective GIS-based incentives and regulatory policies to control and mitigate nutrient pollution of waterbodies.

CHAPTER ?? - ANALYSIS OF INCENTIVE POLICIES FOR PHOSPHORUS RECOVERY. This chapter conduct a research on the design and analysis of incentive policies using the COW2NUTRIENT framework for the implementation of phosphorus recovery technologies at CAFOs minimizing the negative impact in the economic performance of CAFOs. Moreover, the fair allocation of monetary resources when the available budget is limited is studied using the Nash allocation scheme.

1.5.2 *Part II - Nitrogen management and recovery*

CHAPTER ?? - MULTI-SCALE TECHNO-ECONOMIC ASSESSMENT OF NITROGEN RECOVERY SYSTEMS FOR SWINE OPERATIONS. This chapter evaluates the main processes for nitrogen recovery at intensive swine operations. A multi-scale techno-economic analysis is performed to estimate the capital and operating costs for different treatment capacities, identifying the most promising processes.

1.5.3 *Part III - Nitrogen management and recovery*

CHAPTER ?? - OPTIMAL TECHNOLOGY SELECTION FOR THE BIOGAS UPGRADING TO BIOMETHANE. This chapter performs a systematic study of different biogas upgrading to biomethane processes in order to identify the optimal process attending to the particular characteristics of the biogas produced from livestock manure. Food waste and wastewater sludge are also included for comparison. We aimed to determine the optimal biomethane production processes for the potential combination of biomethane production and nutrient recovery processes into an integrated resources recovery facility.

BIBLIOGRAPHY

2

OBJECTIVE

2.1 SCOPE AND OBJECTIVES OF THE THESIS

2.2 MAIN OBJECTIVE

This thesis seeks to promote the recovery and recycling of nutrients contained in livestock waste by identifying the most appropriate technologies for phosphorus and nitrogen recovery at cattle and swine CAFOs, assessing the potential nutrient releases abatement that could be achieved by the deployment of these systems and analyzing incentive policies for their effective implementation at livestock facilities. Moreover, we introduce a systematic framework for evaluating and selecting the most suitable nutrient recovery system at CAFOs considering geospatial environmental vulnerability to nutrient pollution.

2.3 SPECIFIC OBJECTIVES

OBJECTIVE I: To identify the role of intensive farming activities on nutrient pollution, including the main sources of nutrient releases, as well as potential processes and systems for nutrient recovery.

OBJECTIVE II: To identify environmental indicators for nutrient pollution, and use them to assess the potential for the abatement of phosphorus releases by deploying the processes previously selected at livestock facilities at subbasin spatial resolution.

OBJECTIVE III: To develop a decision-support system for the evaluation and selection of nutrient recovery systems at livestock facilities integrating techno-economic data of the nutrient recovery technologies and environmental vulnerability to nutrient pollution information determined through a tailored geographic information system (GIS) in order to select the most suitable system for each particular livestock facility.

OBJECTIVE IV: To design and analyze potential incentive policies for the deployment of phosphorus recovery technologies at livestock facilities, as well as to study the fair allocation of limited monetary resources.

Part I

PHOSPHORUS MANAGEMENT AND RECOVERY

3

ASSESSMENT OF PHOSPHORUS RECOVERY THROUGH THE DEPLOYMENT OF STRUVITE PRECIPITATION SYSTEMS

3.1 INTRODUCTION

Livestock farming and other agricultural activities have altered the natural nutrient cycles. Phosphorus, one of the three plant-grow macronutrients, enters to the global cycle as phosphate rock, which through erosion and chemical weathering is transferred to soils and waterbodies. Also, phosphorus deposited in soils will reach fresh and marine waterbodies by runoff. Phosphorus in rivers is transported to stagnant waterbodies (such as lakes) and oceans, reaching the bottom of lakes and oceans as sediments. The cycle is closed when the buried phosphorus is uplifted again by tectonic processes. Along the cycle, phosphorus can be taken by plants and algae, but after the death of living organisms it returns to the cycle (**RUTTENBERG2001401**). This global natural cycle is largely altered by human activities through the mining and shipping of phosphate rock, mainly for fertilizer production, resulting in unbalanced phosphorus releases to the environment.

Nutrient pollution from anthropogenic sources has become as a critical worldwide water quality problems. Nutrient contamination results in environmental and public health issues as a result of the exponential growth of algae, cyanobacteria, and the occurrence of harmful algal blooms (HABs), which turns into dead zones and hypoxia due to the aerobic degradation of the algal biomass by bacteria; shifting the distribution of aquatic species and releasing toxins in drinking water (**Sampat2**). In addition, the development of HABs and eutrophication processes contributes to climate change through the emission of large amounts of strong greenhouse gases such as CH_4 and N_2O (**Beaulieu**).

However, phosphorus is a limited non-renewable resource, essential nutrient to support life, and widely used as fertilizer to increase crop yields. Actually, phosphorus is one of the most sensitive elements to depletion, as it is a key agricultural fertilizer that has no known substitute. Current global reserves of phosphate rock could be depleted in the next 50 to 100 years (**Cordell**). Therefore, the development of a circular economy around phosphorus capable of recovering the nutrient and reintegrating it into the productive cycle is not only desirable but also a necessary measure to reach sustainable development. Agricultural activities are the main source of nutrients in waterbodies (**Dzombak**), and among them, livestock industry is one of the largest economic sectors. Additionally, the increasing income-spending potential of the middle class in developing countries has increased the demand for dairy and beef products, resulting in the generation of large amounts of livestock organic waste. Considering that an average dairy cow generates 51.19 kg of raw manure per day (**USDAWaste**), the total phosphorus excreted is 11.02 kg per year per animal, equivalent to 5.96 kg of phosphorus as phosphate per year per animal. In the U.S. as of January 2020, a total of 94.4 million head has been reported (**USDACattle2020**). Thus, this shows potential phosphate U.S. releases of $562.6 \cdot 10^6$ kg/yr. **Sampat** presented the link between the presence of livestock facilities and larger concentrations of phosphorus in soil, which potentially can be lost as runoff reaching waterbodies. For animals on pasture, organic waste should not be a resource of concern if stocking rates are not excessive. However, for concentrate animal feeding operations (CAFOs), manure should be correctly managed due to the high rates and spatial concentration of the organic waste generated, representing potential environmental issues. Usually, manure is collected in the animal living zones, and stored as liquid or slurry to be further spread in croplands as nutrient supplementation; or as solid in dry stacking or composting facilities to be sold as compost. Liquid fraction of manure can be also treated in aerobic or anaerobic ponds. However, these approaches do not allow a correct nutrient management since nutrients concentration is variable and not well defined, and nitrogen and phosphorus are unbalanced regarding the nutrient necessities of plans, i.e., if nitrogen demand is covered, there is a surplus in the phosphorus supply which can runoff to waterbodies, and if phosphorus demand is covered, there is a deficit in the nitrogen supply, being necessary to apply additional fertilizers. In addition, during rainy periods the applied manure can runoff, dragging the nutrients contained in it. Nonetheless, phosphorus from liquid cattle waste, either processed in an anaerobic digestion stage or raw waste, can be potentially recovered through different processes (**muhmood2019formation**), reducing the nutrient inputs to waterbodies and its consequential environmental, economic, and social impacts. Among these, it is found that struvite production is one of the most promising cost-effective choices for the recovery of nutrients from cattle waste (**Martin**). Struvite is a phosphate-based mineral, which can be applied as a slow release fertilizer (**Richards**), allowing the redistribution of phosphorus from livestock facilities to nutrient-deficient locations.

Previous studies report struvite formation from different sources of waste, such as municipal wastewater treatment plants (**Battistoni**), mineral fertilizer industry (**Matynia**), or agricultural industry (**Shashvatt**). Thermodynamic models representing the formation of struvite and other precipitates have been also developed for various wastes including liquid swine manure (**celen_using_2007**), human urine (**Harada**; **ronteltap_struvite_2007**), and municipal wastewater (**rahaman_modeling_2014**). Additionally, some complex approaches considering the hydrodynamic and kinetic effects in the formation of struvite have been studied but limited to wastewater treatment (**rahaman_modeling_2014**; **mangin2004fluid**). However, the results obtained from those studies cannot be extrapolated to struvite formation from cattle organic waste, since these residues have some characteristics that hinder struvite formation, including high ionic strength, which reduces the effective concentration of ions; the presence of calcium ions competing for phosphate ions (**Yan**), which inhibits a selective recovery by nutrient precipitation techniques; and the high variability in the manure composition, as a function of the geographical area, the animal feed, etc. (**Tao**). Other controlling factors are the pH level, the magnesium-phosphorus ratio, and the alkalinity of the leachate. Therefore, for an accurate prediction of struvite formation from this waste, it is necessary to include within the thermodynamic model structure for precipitates formation the specific features of cattle waste described above.

In this work, specific surrogate models to predict the production of struvite and calcium precipitates from cattle leachate are developed based on a detailed and robust thermodynamic model. In addition, the variability in the organic waste composition is captured through a probability framework based on Monte Carlo method. The reduced models obtained are used to evaluate the potential of struvite production from cattle waste to mitigate phosphorus releases in watersheds of the United States. Future applications of the developed surrogate models include the development of applications for environmental assessment and the design of policies to prevent nutrient releases, among others.

3.2 METHODS

3.2.1 *Spatial resolution*

A watershed is an area of land which drains all the streams and rainfall to a common drainage, defining the spatial boundaries for the collection of lost elements as runoff. The surface water drainages of the U.S. are identified by the U.S. Geological Survey through the Hydrologic Unit Code system (HUC). The HUC system is a hierarchical system indicated by the number of digits in groups of two, with six levels identified by codes from 2 to 12 digits (i.e., HUC2 to HUC12). These levels refer to regions, subregions, basins, subbasins, watersheds, and subwatersheds. The spatial resolution of this study is the continental United States at watershed scale, considering the boundaries defined by the Hydrologic Unit Code system at 8 digits (HUC8), representing the subbasin level (**HUC8**).

3.2.2 *Assessment of anthropogenic phosphorus from agricultural activities*

3.2.2.1 *Phosphorus releases*

Agricultural emissions are one of the main sources of anthropogenic P releases due to the excessive use of commercial fertilizers and livestock manure for cropland nutrients needs and the uncontrolled nutrient runoff to waterbodies, although for some areas urban source releases can contribute significantly to the total P releases to the environment. However, this analysis is limited to the evaluation of phosphorus releases from agricultural activities (**Dzombak**; **Alexander_2008**; **SPARROW_report_1999**).

Watershed phosphorus releases (E_x) are computed as the sum of the phosphorus releases from fertilizer applications to croplands and from the manure generated by livestock facilities. The releases of phosphorus to each watershed by manure emissions, accounting cattle, swine and poultry, and by fertilizers application, is reported by the IPNI NuGIS project. This is consitent with the most recent data available (year 2014) for fertilizers sales provided by the Association of American Plant Food Control Officials (AAPFCO), fitting the data to HUC8 watershed boundaries. More information about the methodology used for the estimation of agricultural phosphorus releases can be found in (**NuGIS**). Phosphorus content for several commercial phosphate fertilizers and different manure types can be found in **OSU2017** and **OSU2005** respectively.

3.2.2.2 *Phosphorus uptakes*

The elements considered for phosphorus uptake are the crops sown and managed by humans in each watershed. Additionally, the phosphorus retained by wetlands has been considered in the phosphorus balance. The phosphorus uptake by each type of vegetation at watershed level is computed as the product of the land area occupied, the grow yields per area unit and the phosphorus uptake per plant mass unit. Therefore, the total watershed phosphorus uptake (U_x) is computed as the sum of the phosphorus uptake by each type of plant, Eq. 3.1.

$$U_x = \sum^{i} \text{Area}_i \cdot \text{Yield}_i \cdot \text{P}_{\text{uptake } i} \; \forall \; i \; \in \; \text{Plant varieties} \tag{3.1}$$

Since different crops have different phosphorus uptakes and yield rates, the amount of each type of crop is estimated for each watershed. To determine the land cover uses, accounting croplands, pasturelands, wetlands and developed areas (urban areas), information available for the most recent year (2011) from the U.S. Environmental Protection Agency's (U.S. EPA) EnviroAtlas database is used (**EnviroAtlas**). Data from EnviroAtlas is provided with higher spatial resolution, at HUC12 level. To ensure spatial consistency, the data is reconciled at HUC8 level. Once the land uses of each watershed are known, data from the 2017 U.S. Census of Agriculture is used to determine the distribution of crops on croplands, considering corn, soybeans, small grains, cotton, rice, vegetables, orchards, greenhouse and other crops (namely oil crops, sugar crops, and fruits) (**2017CensusofAgriculture**). The data provided by the U.S. Census of Agriculture have a spatial resolution of HUC6. Therefore, it is reconciled at HUC8 level scaling by the area fraction represented by each HUC8 watershed over the total HUC6 hydrologic unit. If two or more crops were harvested from the same land during the year (double cropping), the area was counted for each crop. To determine the nutrients uptake of each type of crop, data from the U.S. Department of Agriculture (USDA) Waste Management field Handbook is considered (**USDAWaste**). For croplands, the specific nutrient uptake values are used for corn, soybeans, cotton, rice and orchards, while average values including the most representative species are used for small grains, vegetables, greenhouse crops, pasture crops, and forest. For pasture lands the average nutrient uptake and crop yield including the main pasture crops: alfalfa, switchgrass and wheatgrass; for forests lands the nutrient uptake and crop yield of Northern hardwoods is considered, and for developed areas null nutrient uptake is considered. The wetlands phosphorus uptake value considered is 0.77 gP m^{-2} year^{-1}, based in the data reported by **Kadlec**.

3.2.2.3 *Phosphorus balance*

To reach environmental sustainability of a productive activity, the releases of phosphorus should be balanced with the phosphorus uptakes from that activity, reducing the impact over the original ecosystems as much as possible. To evaluate the balance of phosphorus releases involved in agricultural activities throughout the U.S. watersheds, the techno-ecological synergy (TES) sustainability metric proposed by **TESmetric** has been considered, Eq. 4.1. A negative value of V_x indicates that the emissions, (E_x), are larger than the uptake capacity of the agricultural activities, (U_x), impacting the ecosystems, while positive values reflect that the releases are lower than the uptake capacity.

$$V_x = \frac{(U_x - E_x)}{E_x} \tag{3.2}$$

3.2.3 *Thermodynamic model for precipitates formation*

The behavior of cattle leachate system has been evaluated through a thermodynamic model, evaluating the formation of different precipitates through chemical equilibrium and material balances, capturing the mutual dependencies based on the competition for the same ions. Four aqueous chemical systems have been considered, water, ammonium, phosphoric acid, and carbonates systems. Moreover, the formation of seven possible precipitates is evaluated: struvite, K-struvite, magnesium hydroxide, calcium hydroxide, calcium carbonate, hydroxyapatite, dicalcium phosphate, and tricalcium phosphate.

3.2.3.1 *Uncertainty in livestock organic waste composition*

The variability in the composition of raw material creates operational difficulties that any material recovery process must deal with. The composition of cattle organic waste depends on multiple factors, among which are livestock feed, geographical area, climate, and other local factors of the livestock operation (**Tao**). Several elements of cattle manure composition play an active role in the formation of struvite and other precipitates. These include the high ionic strength, which reduces the effective concentration of ions; and the distribution ratios between calcium, ammonia and phosphate; and the leachate alkalinity, affecting the chemical equilibrium. To capture the uncertainty generated by the variability in the composition of cattle leachate, 37 data sets of 20 literature references containing the mass fraction of different elements comprising organic livestock waste are evaluated. To estimate feasible cattle leachate compositions, the probability density distribution of each element is calculated by fitting it to the kernel density estimate (KDEs). The selected probability density distributions are normal distribution, as shown in Eq. 3.3, for the distribution of nitrogen, nitrogen as ammonia/total nitrogen ratio, and phosphorus; and lognormal distribution, as defined by Eq. 3.4, for phosphorus as phosphate/total phosphorus ratio, calcium, and potassium. The probability density distribution parameters for each evaluated compound are collected in Table 3.1, where σ is the standard deviation, σ^2 is the variance, μ is the mean of the distribution, M is equal to e^{μ}, and γ is a displacement parameter. Kernel density estimations and probability density distributions for each element evaluated can be found in the Supplementary Material.

The uncertainty in the composition of cattle waste is addressed through the evaluation of the thermodynamic model described in the following sections for multiple cattle waste compositions generated including the probability density distribution of each elements in a Monte Carlo model (**Thomopoulos**).

$$f(x) = \frac{1}{\sqrt{2\pi\sigma}} e^{-\frac{(x-\mu)^2}{2\sigma^2}} \tag{3.3}$$

$$f(x) = \frac{\frac{1}{\frac{x-\gamma}{M}\sigma\sqrt{2\pi}} e^{-\frac{ln\left(\frac{x-\gamma}{M}\right)^2}{2\sigma^2}}}{M} \tag{3.4}$$

Table 3.1: Probability density distributions parameters for cattle organic waste elements.

Param.	Normal distribution			Param.	Lognormal distribution		
	N	$N\text{-}NH_4^+ : N_{total}$	P		$P\text{-}PO_4^{3-} : P_{total}$	Ca	K
μ	0.3841	0.6200	0.04000	M	42.15	0.08000	0.2600
σ	0.1309	0.1250	0.03684	σ	0.0040	0.4500	0.8000
				γ	-41.53	0.04044	0.03389

3.2.3.2 *Initial conditions*

A set of initial conditions must be defined to establish the physico-chemical characteristics of the livestock organic material (**Tao**), see Table 3.2. Please note that pH refers the adjusted pH for optimal struvite precipitation (**Tao**; **Zeng**).

3.2.3.3 *Activities*

Since the cattle waste is a highly non-ideal media due to the high concentrations of dissolved ions, activities instead of molar concentrations are used in the model. Activity coefficients (γ_x) for a element x are calculated using the Debye-Hückel relationship, Eq. 3.6, which relates activity coefficient, temperature, and ionic strength, calculated using Eq. 3.5. Eq. 3.7 is employed to estimate the parameter A (**Tao**; **Metcalf**). Finally, activities for each compound are calculated using Eq. 3.8

Table 3.2: Initial conditions of the livestock organic material system

Variable	Value	Unit
Temperature	298	K
pH	9	-
Electrical conductivity (*EC*)	18,800	$\frac{\mu S}{cm}$
Alkalinity	3000-14500	mg of $CaCO_3$
$[Ca^{2+}]$	0.075-0.175 (determined by Monte Carlo model)	% wt wet
$[K^{+}]$	0.10-0.65 (determined by Monte Carlo model)	% wt wet
$[P\text{-}PO_4^{3-}]$	0.001-0.024 (determined by Monte Carlo model)	% wt wet
$[N\text{-}NH_4^{+}]$	0.015-0.64 (determined by Monte Carlo model)	% wt wet
$[Mg^{2+}]$	0-10	Mg^{2+}/PO_4^{3-} molar ratio

$$I = 1.6 \cdot 10^{-5} \cdot EC, \quad I\,(M)\,,\; EC\left(\frac{\mu S}{cm}\right) \tag{3.5}$$

$$\log_{10}(\gamma_x) = -A \cdot z_x^2 \cdot \left(\frac{\sqrt{I}}{1+\sqrt{I}}\right) - 0.3 \cdot I \tag{3.6}$$

$$A = 0.486 - 6.07 \cdot 10^{-4} \cdot T + 6.43 \cdot 10^{-6} \cdot T^2, \quad T(K) \tag{3.7}$$

$$\{x\} = [x] \cdot \gamma_x \tag{3.8}$$

3.2.3.4 *Distribution of species in aqueous phase*

The distribution of species for ammonia, water, phosphoric acid, and carbonate systems in cattle leachate is determined by chemical equilibria:

$$\sum_j n_j Reactant_j \leftrightarrow \sum_k m_k Product_k \tag{3.9}$$

where n_j and m_k are the stoichiometric coefficients of the reactants and products respectively, and defining J as the set of chemical systems described in Table 3.3 for water, ammonia, and phosphoric acid systems, the thermodynamic equilibrium is defined for all the elements of the set as shown in Eq. 3.10. In combination with the material balances, Eq. 3.11, these define the chemical equilibrium for all the elements of the set. The description of the model for carbonate system is detailed in the Supplementary Material, and pK values are collected in Table 3.3.

$$K_J = \frac{\left(\prod_k \{Products\}_k^{m_k}\right)_J}{\left(\prod_j \{Reactants\}_j^{n_j}\right)_J} \tag{3.10}$$

$$[i]_J^{initial} = \sum_J [Compounds]_J \tag{3.11}$$

$$i \in \{NH_4^+,\ Ca^{2+},\ Mg^{2+},\ PO_4^{3-},\ CO_3^{2-}\}$$

Table 3.3: pK_{sp} values for the considered aqueous phase chemical systems.

Name	Chemical system	pK	Source
Ammonia	$NH_4^+ \leftrightarrow NH_3 + H^+$	9.2	(**Bates**)
Water	$H_2O \leftrightarrow OH^- + H^+$	14	(**Skoog**)
Phosphoric acid	$H_3PO_4 \leftrightarrow H_2PO_4^- + H^+$	2.1	(**Ohlinger**)
	$H_2PO_4^- \leftrightarrow HPO_4^{2-} + H^+$	7.2	(**Ohlinger**)
	$HPO_4^{2-} \leftrightarrow PO_4^{3-} + H^+$	12.35	(**Ohlinger**)
Carbonic acid	$H_2CO_3 \leftrightarrow HCO_3^- + H^+$	6.35	(**Skoog**)
	$HCO_3^- \leftrightarrow CO_3^{2-} + H^+$	10.33	(**Skoog**)

3.2.3.5 *Precipitates formation*

The precipitates that can be potentially formed from cattle waste have been selected based on the precipitates reported by previous studies (**Tao**; **Harada**; **gadekar2010validation**). A general solubility equilibrium, where n_a and m_b are the stoichiometric coefficients of the reactants and solid products respectively, can be written as:

$$\sum_b m_b Precipitate_b \downarrow \leftrightarrow \sum_a n_a Reactant_a \tag{3.12}$$

The solid species considered in this study and their corresponding pKsp values are shown in Table 3.4. These are the main precipitates that can be formed from the ions found in the cattle leachate. Considering the activity of solid species is equal to 1, and defining L as the set of chemical systems described in Table 3.4, the solubility equilibrium is defined for all the elements of the set as shown in Eq. 3.13.

The supersaturation index (Ω) is the defined as the ratio between the ion activity product and the solubility product (Ksp), as shown in Eq. 3.14

Table 3.4: Solids species considered in this work.

Name	Chemical system	pK_{sp}	Source
Struvite	$MgNH_4PO_4 \cdot 6H_2O \leftrightarrow Mg^{2+} + NH_4^+ + PO_4^{3-}$	13.26	(**Ohlinger**)
K-struvite	$MgKPO_4 \cdot 6H_2O \leftrightarrow Mg^{2+} + K^+ + PO_4^{3-}$	10.6	(**TaylorAW**)
Hydroxyapatite	$Ca_5\left(PO_4\right)_3 OH \leftrightarrow 5Ca^{2+} + 3PO_4^{3-} + OH^-$	44.33	(**Brezonik**)
Calcium carbonate	$CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-}$	8.48	(**Morse**)
Tricalcium phosphate	$Ca_3\left(PO_4\right)_2 \leftrightarrow 3Ca^{2+} + 2PO_4^{3-}$	25.50	(**Fowler**)
Dicalcium phosphate	$CaHPO_4 \leftrightarrow Ca^{2+} + HPO_4^{2-}$	6.57	(**Gregory**)
Calcium hydroxide	$Ca\left(OH\right)_2 \leftrightarrow Ca^{2+} + 2OH^-$	5.19	(**Skoog**)
Magnesium hydroxide	$Mg(OH)_2 \leftrightarrow Mg^{2+} + 2OH^-$	11.15	(**Skoog**)

(**Tao**). Therefore, the value of Ω determines if a compound precipitates. A saturation index $\Omega > 1$ indicates supersaturated conditions where precipitate may form, $\Omega = 1$ indicates equilibrium between solid and liquid phases, and $\Omega < 1$ indicates unsaturated conditions where no precipitate can form.

The higher value of the supersaturation index, the larger formation potential of a precipitate. Therefore, the sequence for the precipitation of different species can be set by comparing the supersaturation index values. The amount of solid species generated is computed through material balances, Eq. 3.15.

$$K_{sp_L} = \left(\prod \{Reactants\}_a^{n_a}\right)_L \tag{3.13}$$

$$\Omega_L = \frac{\left(\prod \{Reactants\}_a^{n_a}\right)_L}{K_{sp_L}} \tag{3.14}$$

$$[i]_L^{initial} = \sum_L [Compounds]_L \tag{3.15}$$

$$i \in \left\{NH_4^+,\ Ca^{2+},\ Mg^{2+},\ PO_4^{3-},\ CO_3^{2-}\right\}$$

3.2.3.6 *Thermodynamic model algorithm*

Figure 3.1 shows a flowchart describing the proposed algorithm to solve the thermodynamic model of solid compound formation in cattle organic waste. In step *a*, the operating conditions and the initial molar concentrations of Ca^{2+}, K^{+}, Mg^{2+}, NH_4^{+}, and PO_4^{3-} in cattle leachate are defined as described previously. In step *b*, ionic strength and activity coefficients are computed. Next, in steps *c* and *d*, two parallel problems are solved, the equilibrium of the aqueous species, and the alkalinity problem to determine the distribution of carbonates. After determining the concentration of all species in the organic waste, the supersaturation index for all species is computed in step *e*. The compound with the maximum supersaturation index is assumed to precipitate first. The amount of formed precipitate is computed by solving the solubility equilibrium and the material balance. As a result of the precipitate formation, the concentration of some species in aqueous phase is reduced. Therefore, the equilibrium of the aqueous species and the alkalinity problem must be recalculated, to obtain the new concentration values of the different compounds in the waste, and the iterative process, starts again.

The iterative process runs until each component saturation index is equal or less than one, and the formation of the precipitates stops.

3.2.3.7 *Integration of waste composition uncertainty and precipitates formation thermodynamic models*

The evaluation of livestock waste variability in the formation of struvite and other precipitates, consists of 5 steps, as shown in Fig. 3.2. First, cattle waste composition data are collected from literature. Using these data, probability density distributions for the compounds of cattle leachate are estimated, and they are used in the Monte Carlo model to obtain feasible composition data sets of cattle organic waste. Random points are generated for each chemical compound and species ratios (i.e. N, P, K, Ca, N-NH_4^{+} : N_{total}, and P-PO_4^{3-} : P_{total}). Finally, the thermodynamic model is solved for the composition data sets generated, obtaining the precipitated compounds formed.

The thermodynamic model has been implemented in the algebraic modeling language JuMP, embedded in the programming language Julia (**DunningHuchetteLubin2017**; **bezanson2017julia**). The statistical study of cattle waste composition data, the Monte Carlo framework, result analysis, and data visualization were made in Python language (**Python**; **Numpy**; **Matplotlib**; **Pandas**).

3.2.3.8 *Model validation and limitations*

The developed model was validated using the data provided by **Zeng**. Their work was carried out under similar operational conditions to which this work intends to evaluate. In Fig. 3.3 experimental and model results are compared. The values at high Mg^{2+} molar ratio, when the largest supersaturation values are reached and the formation of struvite is close to the maximum allowed by the thermodynamic equilibrium, match the experimental data. However, at lower ratios, differences between results of the thermodynamic model proposed and experimental data can be observed. As the authors of the article indicate, this differences can be due to the presence of many suspended solids which interfere in the struvite formation process. Note that this work is focused on the thermodynamic aspect, without considering other aspects such as chemical kinetics or transport phenomena. The scarcity of data is an impediment to further validate the model.

In addition to the lack of previous studies and data availability to evaluate the effects of kinetics and transport phenomena in the formation precipitates from cattle leachate, another improvement of the proposed model can be achieved by the experimental determination of pKsp values for the potential precipitates formed from cattle leachate. For struvite, the selected pKsp value is taken from the work of **Ohlinger**, as they determined the pKsp value for struvite formation in digestate, a medium with high organic load and dissolved elements like cattle leachate. Otherwise, when pKsp data for cattle waste is unavailable from previous studies, the reported values for water are used. A limitation in the use of the obtained surrogate models is that the formation of struvite and calcium precipitates can only be determined for cattle waste. Although a general formulation for the thermodynamic model is used, and the methodology proposed to include the effect of the uncertainty is not restricted to the use of a specific waste, only cattle leachate has been considered in this study. However, if data on the composition is available, surrogate models to predict the formation of struvite and calcium precipitates from other waste sources can be easily developed.

3.3 RESULTS AND DISCUSSION

3.3.1 *Surrogate models to estimate the formation of precipitates from livestock organic waste*

The influence of the main controllable parameters for struvite production at industrial scale operation was evaluated: the presence of magnesium and calcium, and the alkalinity. Surrogate models were developed to allow the analytical estimation of precipitates formation. pH value for the struvite precipitation process has been considered as a fixed variable, since there is a wide consensus about a pH value of 9, at which struvite solubility is minimum, is optimal, enhancing the phosphorus and nitrogen conversion to struvite and its eventual precipitation (**Tao**; **Zeng**).

3.3.1.1 *Influence of magnesium*

In phosphorus recovery processes through struvite formation, magnesium is usually added to increase the saturation of struvite, enhancing its precipitation. This is especially important for cattle leachate due to the high presence of calcium ions competing with other cations for phosphate anions, and the high ionic strength of livestock leachate, reducing the effective concentration of ions. If the supplementation of magnesium provides enough magnesium ions, struvite will reach higher supersaturation ratio than calcium precipitates, leading the formation of struvite over calcium compounds. To estimate the performance of struvite precipitation from cattle leachate, the developed thermodynamic model was solved for 50 different composition data sets. The average alkalinity value of the range reported by **Tao** is considered, 8770.5 mg of $CaCO_3$. The plots showing evolution of precipitates formation in function of the Mg^{2+}/PO_4^{3-} molar ratio are collected in the Supplementary Material. Analyzing the average fraction of PO_4 recovered in form of struvite as a function of the Mg^{2+}/PO_4^{3-} molar ratio, a tentative value for Mg^{2+}/PO_4^{3-} molar ratio between 2 and 4 can be set as a compromise effectiveness-cost solution. Higher values result in a considerable consumption of magnesium returning lower improvements in phosphate recovery as struvite. The surrogate model obtained to evaluate performance of struvite precipitation in function of the magnesium supplied is a Monod type equation, as shown in Eq. 3.16, where $x_{Mg^{2+}:PO_4^{3-}}$ is referred to the Mg^{2+}/PO_4^{3-} molar ratio.

$$x_{\text{struvite}(PO_4^{3-})} = \frac{0.957 \cdot x_{Mg^{2+}:PO_4^{3-}}}{0.996 + x_{Mg^{2+}:PO_4^{3-}}} \tag{3.16}$$

The evolution in the formation of calcium precipitates as a function of the Mg^{2+}/PO_4^{3-} molar ratio was also studied. Hydroxyapatite and calcium carbonate are the only calcium precipitates produced. Both hydroxyapatite and $CaCO_3$ patterns can be related to the increment of struvite formation along the increase of Mg^{2+}/PO_4^{3-} molar ratio values, which reduces the presence of phosphate ions, and consequently decreases the supersaturation of hydroxyapatite. Therefore, there are more calcium ions available to form calcium carbonate. Surrogate models fit to first order polynomial equations for hydroxyapatite, Eq. 3.18, and for calcium carbonate, Eq. 3.17.

$$x_{\text{hydroxyapatite}(Ca^{2+})} = -1.299 \cdot 10^{-2} \cdot x_{Mg:PO_4^{3-}} + 0.248 \tag{3.17}$$

$$x_{CaCO_3(Ca^{2+})} = 1.296 \cdot 10^{-2} \cdot x_{Mg:PO_4^{3-}} + 0.749 \tag{3.18}$$

3.3.1.2 *Influence of calcium*

One of the hindrances of cattle leachate for struvite precipitation is the presence of calcium ions competing with other cations for phosphate to form different precipitates. To study the inhibitory influence of calcium in cattle leachate for struvite precipitation, the thermodynamic model was evaluated for the same 50 different composition data sets used in the previous study along Ca^{2+}/PO_4^{3-} molar ratio values from 0 to 5. To exclude the influence of magnesium concentration, the study was carried out fixing the Mg^{2+}/PO_4^{3-} molar ratio at 2. The plots showing evolution of precipitates formation in function of the Ca^{2+}/PO_4^{3-} molar ratio are collected in the Supplementary Material.

The phosphorus as phosphate fraction recovered as struvite exhibits a steep descent at Ca^{2+}/PO_4^{3-} values between 0 and 2, followed by an asymptotic behavior tending to 0. The dispersion of the values has slight variations along with the evaluated Mg^{2+}/PO_4^{3-} values. For hydroxyapatite and calcium carbonate, the higher Ca^{2+}/PO_4^{3-} value, the greater dispersion for the obtained values. This is due to the increase in the supersaturation values for both calcium precipitates because of the presence of a higher number of calcium ions in the leachate.

The surrogate models obtained for struvite and calcium carbonate fit pseudo-sigmoidal equations, Eqs. 3.19 and 3.21 respectively; while for hydroxyapatite (HAP) is a second polynomial function, Eq. 3.20. In all cases, $x_{Ca^{2+}:PO_4^{3-}}$ is referred to Ca^{2+}/PO_4^{3-} molar ratio.

$$x_{\text{struvite}(PO_4^{3-})} = \frac{0.798}{1 + \left(x_{Ca^{2+}:PO_4^{3-}} \cdot 0.576\right)^{2.113}} \tag{3.19}$$

$$x_{\text{hydroxyapatite}(Ca^{2+})} = -4.321 \cdot 10^{-2} \cdot x^2_{Ca^{2+}:PO_4^{3-}} + 0.313 \cdot x_{Ca^{2+}:PO_4^{3-}} - 3.619 \cdot 10^{-2} \tag{3.20}$$

$$x_{CaCO_3(Ca^{2+})} = \frac{1.020}{1 + \left(x_{Ca^{2+}:PO_4^{3-}} \cdot 0.410\right)^{1.029}} \tag{3.21}$$

3.3.1.3 *Influence of alkalinity*

Alkalinity is a parameter which can be used to control the production of calcium precipitates. When the presence of carbonates is low, the competition between hydroxyapatite and calcium carbonate tends to benefit the first compound because the limited availability of carbonate ions reduces the supersaturation of calcium carbonate. However, the predominance of hydroxyapatite reduces the formation of struvite since both elements compete for phosphate ions. Therefore, the presence of significant amounts of carbonates (performing at alkaline conditions) reduces the formation of hydroxyapatite and promotes the formation of struvite.

The results for the formation of struvite, hydroxyapatite and calcium carbonate considering the same 50 different composition data sets used in the previous studies in function of the alkalinity are collected in the Supplementary Material. It can be observed that the behavior of struvite formation and calcium carbonate are related, with an abrupt change for both elements at alkalinity values between 3,000 and 4,000 mg of $CaCO_3$, reaching plateaus beyond these values. The dispersion of values follow a similar pattern for both struvite and calcium carbonate, being lower at low alkalinity values, and progressively growing until reaching a value of 4,000 mg of $CaCO_3$. Beyond this value, the dispersion of values remains constant. Hydroxyapatite formation decrease continuously along the alkalinity values, being complementary with the formation of calcium carbonate.

Therefore, struvite formation from livestock leachate can be enhanced inhibiting hydroxyapatite formation by controlling the alkalinity level, increasing the formation of calcium carbonate and reducing the concentration of calcium ions competing for phosphate. Pseudo-sigmoidal fits are shown in Eq. 3.22 for $x_{struvite\left(PO_4^{3-}\right)}$, Eq. 3.23 for the case of hydroxyapatite, and Eq. 3.24 for calcium carbonate, where x_{Alk} is referred to alkalinity (mg $|CaCO_3$).

$$x_{\text{struvite}\left(\text{PO}_4^{3-}\right)} = \frac{0.695}{1 + \left(x_{\text{Alk}} \cdot 4.229 \cdot 10^{-4}\right)^{-2.638}} \tag{3.22}$$

$$x_{\text{hydroxyapatite}\left(\text{Ca}^{2+}\right)} = \frac{0.260}{1 + \left(x_{\text{Alk}} \cdot 6.460 \cdot 10^{-5}\right)^{3.390}} \tag{3.23}$$

$$x_{\text{CaCO}_3\left(\text{Ca}^{2+}\right)} = \frac{0.847}{1 + \left(x_{\text{Alk}} \cdot 4.646 \cdot 10^{-4}\right)^{-1.870}} \tag{3.24}$$

3.3.1.4 *Interactions between calcium and magnesium to phosphate ratios*

Interactions between calcium and magnesium to phosphate ratios were evaluated to determine a target operational area for optimal struvite production performance. In Fig. 3.4 the formation of struvite as function of Mg^{2+}/PO_4^{3-} and Ca^{2+}/PO_4^{3-} molar ratios is shown, where the area with the highest phosphate recovery in form of struvite has been shaded. It can be observed that struvite formation depends strongly on the Ca^{2+}/PO_4^{3-} molar ratio. For Ca^{2+}/PO_4^{3-} values less than 3 struvite formation reaches the maximum values, even for low Mg^{2+}/PO_4^{3-} molar ratio values. For high calcium/phosphate ratios, struvite formation decreases abruptly, obtaining low increases in struvite formation even for large supplies of magnesium.

3.3.2 *Phosphorus releases from cattle leachate potentially avoided via struvite formation*

Phosphorus pollution of waterbodies, followed by eutrophication and hypoxia scenarios, represents a major environmental problem for the current societies. Considering the United States, the Census of Agriculture reports more than 93 million of cattle heads (**2017CensusofAgriculture**), generating an estimated amount of 1,144 million of tons of organic waste per year. The phosphorus contained in the organic waste can be lost as runoff, reaching waterbodies, and polluting the surrounding aquatic ecosystems. Actually, several outstanding cases of eutrophication have taken place in the U.S. in recent times, such as the events occurred in Lake Erie since 1990, and the dead zone in the Gulf of Mexico because of in-excess nutrients discharges collected along the Mississippi River basin. Therefore, nutrient recovery strategies must be implemented to capture phosphorus (and nitrogen) before reaching the waterbodies. Additionally, phosphorus recovery as struvite allows its redistribution to nutrient deficient areas (**Martin**). The surrogate models developed are used to estimate the potential phosphorus emissions avoided in each watershed through phosphorus recovery from cattle leachate as struvite.

3.3.2.1 *Balance of phosphorus involved in agricultural activities throughout the U.S. watersheds*

To reach environmental sustainability and reduce the impact over the original ecosystems as much as possible, the releases of phosphorus should be balanced with a coordinated network of phosphorus uptakes. To determine the balance between the releases and uptakes of phosphorus from the agricultural sector, the TES sustainability metric is computed for each watershed in the U.S., showing the watersheds where the phosphorus releases are unbalanced and impacting the environment, Fig. 3.5. For a total of 2,104 HUC8 watersheds, data is unavailable for 6 watersheds, the phosphorus releases and uptakes are balanced in 1,410 watersheds, and 691 exhibit unbalanced phosphorus releases, representing the 33.12% of total watersheds. It can be observed a larger concentration of unbalanced watersheds along the Mississippi River basin and around the Lake Erie, areas currently affected by eutrophication issues.

For studies requiring higher spatial resolution, more accurate values for the TES metric can be stimated through the use of local inventories for phosphorus releases and uptakes. A dataset with the phosphorus releases and uptakes, the phosphorus balance, and the TES metric computed for each watershed are available in the Supplementary Material. A dataset with the phosphorus releases and uptakes, the phosphorus balance, and the TES metric computed for each watershed are available in the Supplementary Material.

3.3.2.2 *Phosphorus recovered from cattle leachate through struvite precipitation*

Since the scope of the surrogate models developed is limited to the treatment of cattle leachate, only P releases from cattle organic waste will be considered for recovery. Additionally, as it is mentioned in the description of the model, only the phosphate fraction of phosphorus can be recovered through struvite precipitation. Data provided by IPNI NuGIS (**NuGIS**) report total manure generated, but do not report the breakdown of manure generated by different livestock sources. Therefore, the inventory of cattle for each HUC6 watershed reported by the U.S. Census of Agriculture is used (**2017CensusofAgriculture**). To keep spatial consistency between data, the inventory of cattle was aggregated from HUC6 to HUC8 watershed level scaling by the fraction of area represented by each HUC8 basin over the total HUC6 area. The breakdown of cattle types in the U.S. Census of Agriculture is not available at watershed level, but it is available at state level. Therefore, the number of cattle heads is weighted by the fraction of milk and beef animals in the corresponding state. finally, the animals number for each type of cattle is calculated using the normalization values provided by Kellog et al. (2010) (**Kellog2000**). If the watershed is shared among several states, the average of the represented states is considered.

Since the supply of magnesium is the easiest controllable variable in the struvite precipitation process, the scenarios evaluated to determine the phosphorus emissions avoided through struvite precipitation were defined through the use of different amounts of magnesium using the surrogate model shown in Eq. 3.16. The different supplies of magnesium have a direct influence on the economy of the process, being one of the highest operating costs items. A summary of the scenarios evaluated and the results obtained is presented in Table 3.5. The fraction of phosphorus releases avoided is computed over the total phosphorus releases from agricultural activities, including manure releases and fertilizer application, as described in Section 3.2.2.1.

Table 3.5: Scenarios considered and results for cattle leachate phosphorus recovery

Scenario	1	2	3	4
Mg^{2+}/PO_4^{3-} molar ratio	1	2	4	6
Total P releases avoided (total watersheds) (tons)	422,104	562,430	674,556	722,573
Average P releases avoided (total watersheds) (%)	22.63	30.16	36.17	38.75
Average P releases avoided (unbalanced watersheds) (%)	18.07	24.08	28.88	30.94
kg Mg/kg $P_{recovered}$	2.68	4.02	6.71	9.40

The results for each scenario considered at watershed scale are shown in Fig. 3.6, where darker colors represent larger phosphorus releases avoided. It can be observed that struvite production can contribute to reducing phosphorus emissions around Lake Erie and the Great Lakes region, one of the most severely affected areas by eutrophication problems. Additionally, other areas where the phosphorus emissions avoided are especially significant are the upper basin of the Mississippi River, and the basins located in the south-central region of the United States, such as the areas of some tributaries rivers to the Mississippi River basin, the Rio Grande river and the Colorado River basin. At national level, struvite production can contribute to reduce the agricultural phosphorus releases by 22% for most conservative case where the lowest amount of magnesium is added. The phosphorus fraction recovered raises until a 30% and 36% when the amount of magnesium added is multiplied by 2 and by 4 respectively. However, for the scenario 4 the increase in the supply of magnesium only increases the phosphorus recovered in 2 percentual points compared with the previous scenario. Therefore, the implementation of struvite production processes for phosphorus recovering in cattle facilities can contribute significantly to the reduction in the phosphorus emissions from agricultural operations, reducing the runoffs to waterbodies and mitigating the nutrient pollution of the aquatic ecosystems. However, when only unbalance watersheds are considered, the average fraction of phosphorus releases avoided decreases, suggesting that, from a global overview, the phosphorus releases due to fertilizers play a major role in these watersheds than when balance and unbalance watersheds are evaluated altogether. Data at watershed level are collected in the Supplementary Material.

Therefore, the phosphorus recovered from livestock facilities have a significant impact in the reduction of phosphorus releases to the environment. However, to achieve a successful implementation of nutrient management strategies, coordinated network management efforts to mitigate nutrient pollution of aquatic systems including point and non-point sources, should be performed for optimizing nutrient management programs that minimize the capital and operating costs while maximizing the environmental benefits. Proposals for the development of coordinated management systems for organic wastes have been presented by **Sharara**, **Sampat3**, and **hu_logistics_2019**.

3.4 CONCLUSIONS

To estimate the potential phosphorus releases avoided through struvite precipitation from cattle waste, a thermodynamic framework has been developed to evaluate struvite production from cattle organic waste as a technology for nutrient management and recovery. A set of practical numerical correlations is developed to help predict the struvite recovery. Cattle waste treatment and nutrient recovery through struvite formation is a feasible process from a thermodynamic perspective, reaching phosphate recovery efficiencies up to 80% with the addition of considerable amounts of magnesium. Additionally, the results show that alkaline conditions can control the calcium ions when their presence in the medium is high and these can interfere in the formation of struvite by precipitating the calcium ions as calcium carbonate, and enhancing the recovery of phosphate as struvite. However, the variability in the organic waste composition is an important parameter that has a high impact on the efficiency of the process. Therefore, an individual composition analysis of the treated cattle waste should be the ideal procedure to achieve the optimal performance of the process by adjusting the operating conditions, particularly the amount of magnesium added and the alkalinity of the medium. Nevertheless, there are opportunities for improving the proposed model by the experimental determination of pKsp values for all potential precipitates from cattle leachate, and by including the effects from kinetics and transport phenomena.

The techno-ecological synergy sustainability metric (TES) is a useful tool for visualizing the spatial distribution of environmental problems, making it possible to determine what areas are more sensible to nutrient pollution, and allowing an adequate distribution of efforts to mitigate phosphorus releases and achieved better nutrient management practices. In the U.S., struvite production has large potential for reducing the phosphorus losses from livestock facilities, avoiding between the 22% and the 36% of the phosphorus releases from the agricultural sector at national level, reducing the phosphorus runoff and mitigating the nutrient pollution of waterbodies. In addition, it can be observed how struvite production can significantly contribute to reducing phosphorus emissions around Lake Erie and the Great Lakes region, some of the most severely affected areas by eutrophication problems. It should be remarked that the production of struvite from cattle leachate allows the redistribution of phosphorus to nutrient deficient areas reducing the phosphorus runoff to waterbodies and mitigating the nutrient pollution of aquatic ecosystems. However, future research is needed to consider temporal aspects, transportation logistics, and coordinated management strategies for achieving global solutions to global problems.

NOMENCLATURE

Variables

A	parameter of the Debye-Hückel relationship
EC	electrical conductivity $\left(\frac{\mu\text{S}}{\text{cm}}\right)$
E_x	emissions of component x
I	ionic strength (M)
K	thermodynamic equilibrium constant
K_{sp}	solubility product
M	equal to e^{μ}
T	temperature (K)
U_x	uptakes of component x
V_x	techno-ecological synergy sustainability metric for component x
Ω	supersaturation ratio
γ	displacement parameter

γ_x	activity coefficient for a element x
μ	mean of the distribution
σ	standard deviation
σ^2	variance
m	stoichiometric coefficient
n	stoichiometric coefficient
x_{Alk}	alkalinity (mg $CaCO_3$)
x_{CaCO_3}	fraction of calcium recovered as calcium carbonate
$x_{Ca^{2+}:PO_4^{3-}}$	Ca^{2+}/PO_4^{3-} molar ratio
$x_{Mg^{2+}:PO_4^{3-}}$	Mg^{2+}/PO_4^{3-} molar ratio
$x_{hydroxyapatite(Ca^{2+})}$	fraction of calcium recovered as hydroxyapatite
$x_{struvite\left(PO_4^{3-}\right)}$	fraction of phosphorus as phosphate recovered as struvite
z_x	integer charge of ion x

Abbreviations

AAPFCO	Association of American Plant Food Control Officials
CAFO	Concentrated Animal Feeding Operation
HAB	Harmful Algal Bloom
HUC	Hydrologic Unit Code
KDE	Kernel Density Estimation
USDA	United States Department of Agriculture

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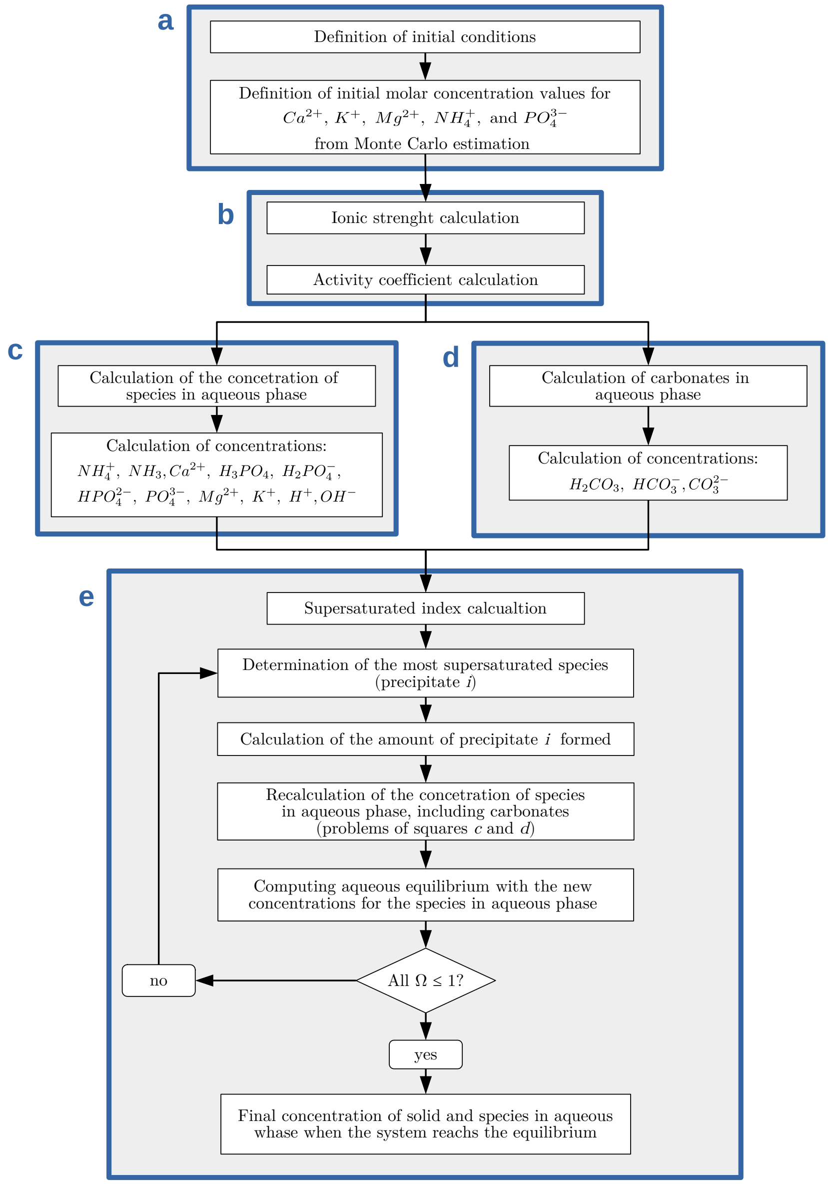


Figure 3.1: Flowchart of the proposed algorithm to solve the thermodynamic model for the formation of precipitates in cattle organic waste.

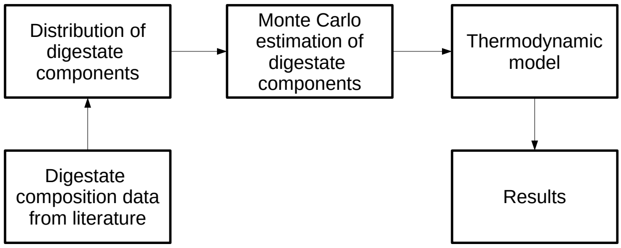


Figure 3.2: A solution procedure to evaluate the influence of the cattle waste composition variability in the formation of struvite.

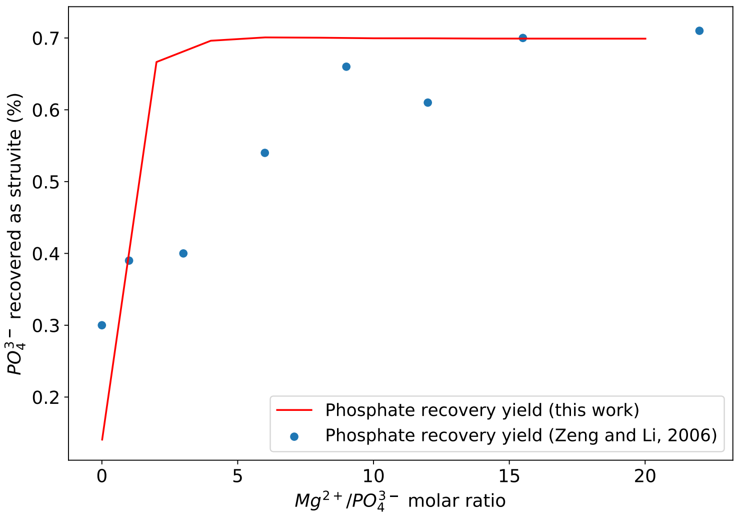


Figure 3.3: Comparison between experimental results reported by **Zeng** and the results provided by the model developed in this work.

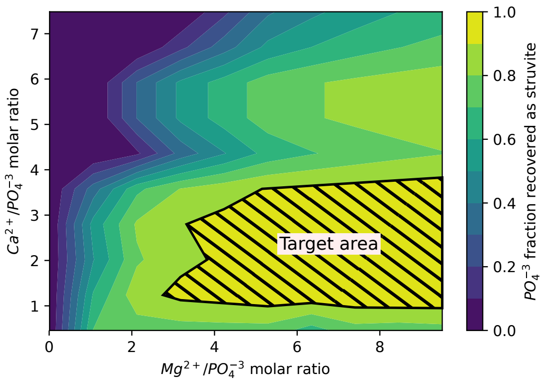


Figure 3.4: Influence of magnesium and calcium in struvite precipitation.

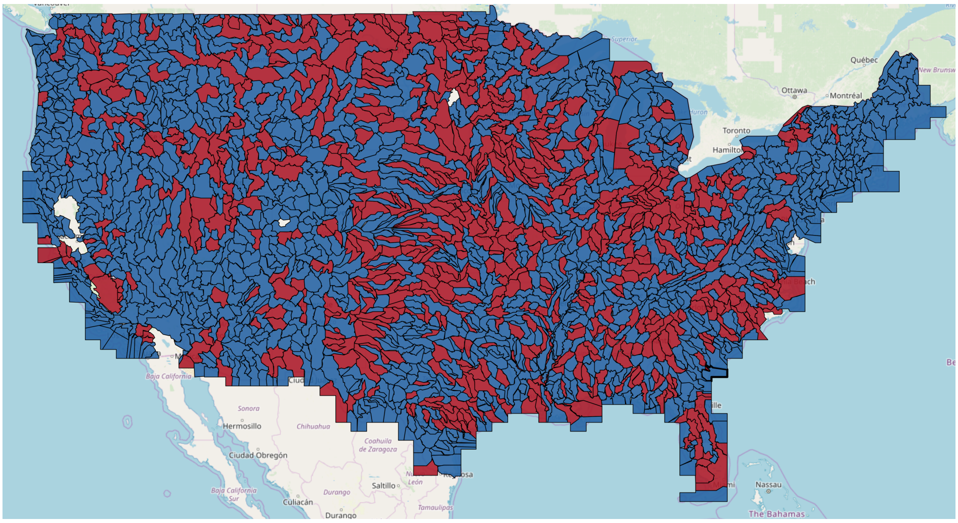
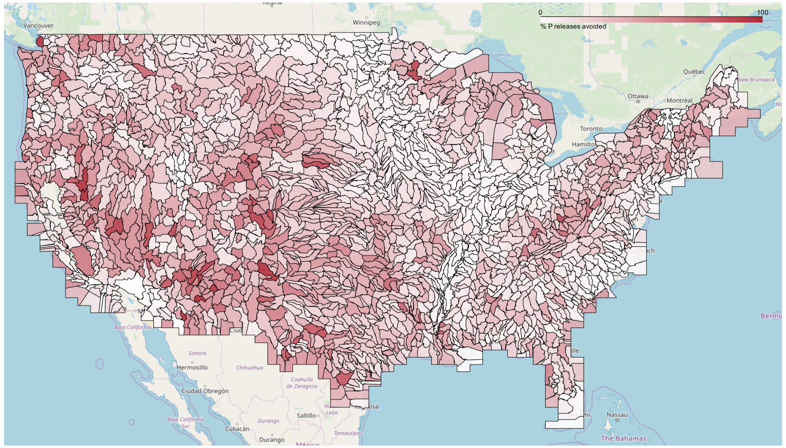
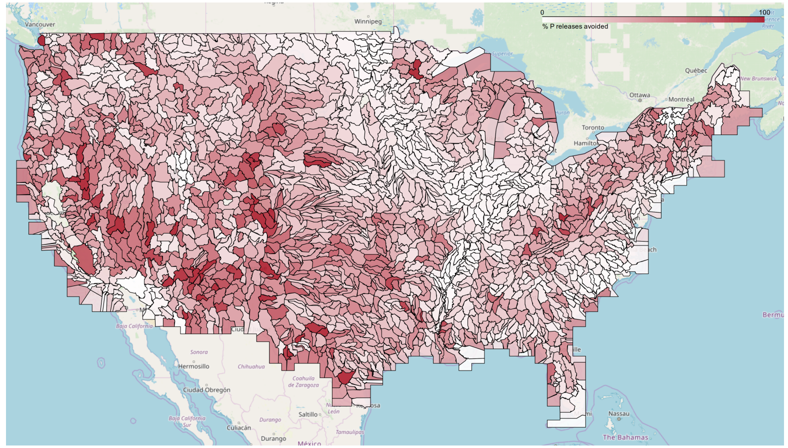


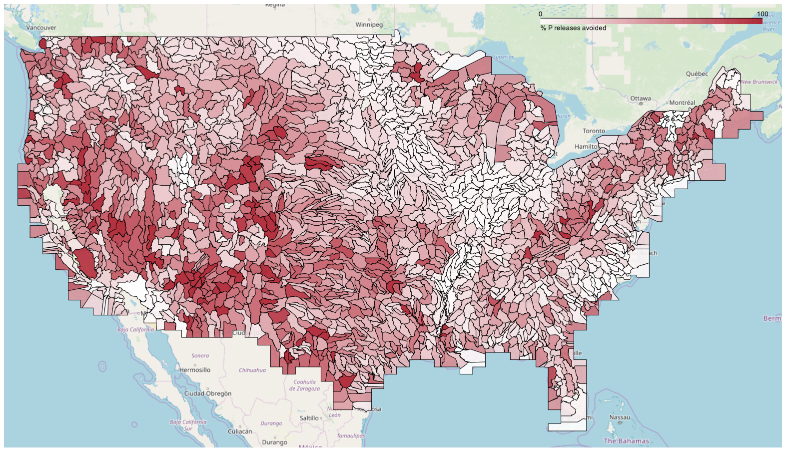
Figure 3.5: Techno-ecological synergy (TES) metric values for HUC8 watersheds. Red indicates watersheds with unbalanced agricultural phosphorus releases, and blue indicates watersheds with balanced agricultural phosphorus releases. White indicates watersheds with not available data.



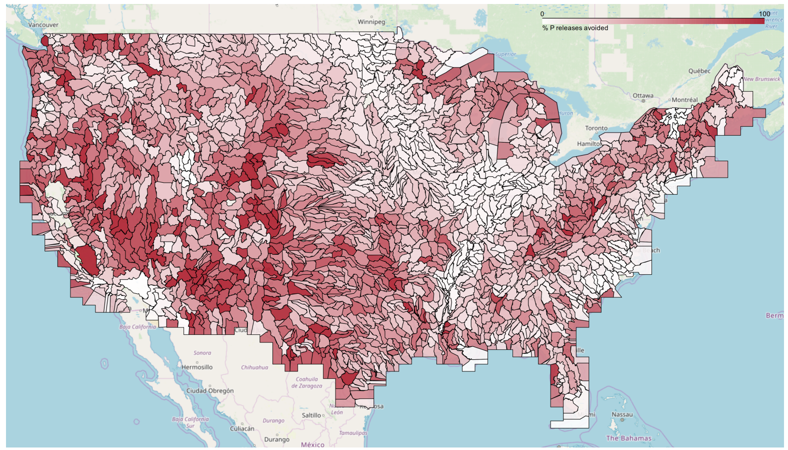
(a) Scenario 1



(b) Scenario 2



(c) Scenario 3



(d) Scenario 4

Figure 3.6: Phosphorus releases avoided through struvite production for the different scenarios considered. Darker colors represent larger phosphorus recovery

4

GEOSPATIAL ENVIRONMENTAL AND TECHNO-ECONOMIC FRAMEWORK FOR SUSTAINABLE PHOSPHORUS MANAGEMENT AT LIVESTOCK FACILITIES

4.1 INTRODUCTION

Phosphorus is a source of concern for modern societies. On the one hand, nutrient pollution of waterbodies is one of the major water quality problems worldwide, resulting in environmental issues as a consequence of the eutrophication of waterbodies, and the occurrence of cyanobacteria and harmful algal blooms (HABs). Surveys reveal that eutrophication is a global problem, reporting that 54% of lakes in Asia, 53% in Europe, 48% in North America, 41% in South America, and 28% in Africa are eutrophic (**ansari_eutrophication_2010**). In addition to eutrophication, hypoxia of aquatic ecosystems is associated with the aerobic degradation of the algal biomass by bacteria, shifting the distribution of aquatic species and releasing toxins in drinking water sources (**sampat_economic_2018**). Although eutrophication is affected by several factors, such as temperature and the self-purification capacity of waterbodies, the primary limiting factor for eutrophication is often the phosphate concentration (**Ullmanns**). Aside from disturbing aquatic ecosystems, eutrophication also contributes to climate change, emitting large amounts of strong greenhouse gases as a consequence of the biomass degradation, such as CH_4 and N_2O (**beaulieu_eutrophication_2019**). On the other hand, phosphorus is an essential nutrient for living organisms, and a key element for maintaining agricultural productivity. However, phosphorus is a resource very sensitive to depletion, since extractable deposits of phosphorus rock are limited and there is no known substitute or synthetic replacement. Projections estimate limited availability of phosphate over the next century (**cordell_story_2009**). Therefore, in addition to the environmental perspective, the search for phosphorus recycling processes is a major driving force for the development of nutrient recovery systems (**reijnders2014phosphorus**).

Agricultural activities are one of the main contributors to human-based phosphorus releases (**Dzombak**), including non-point source releases by over-use of fertilizers in croplands, point source releases originated from the disposal of livestock waste, and nutrient legacy that have accumulated in watersheds due to historical phosphorus releases. Focusing on the point source releases generated by the cattle industry, these result from the production of large amounts of livestock organic waste, containing substantial amounts of phosphate and ammonia. **Sampat2017** presented the link between the presence of livestock facilities and higher concentrations of phosphorus in soil, resulting in increased nutrient runoff to waterbodies. While for animals on pasture, organic waste should not be a source of concern if stocking rates are not excessive, for concentrated animal feeding operations (CAFOs) manure should be properly managed due to the high rates and spatial concentration of the organic waste generated. A common practice to recycle the nutrients contained in the organic waste is the land application of the manure. However, since the high-water content of manure makes its transportation to nutrient deficient locations difficult and expensive, it is usually spread in the surroundings of the CAFOs, leading to surplus of nutrients in soils and phosphorus runoff to waterbodies (**USDAHandbook**).

The implementation of nutrient recovery technologies at livestock facilities to recover phosphorus from cattle manure is a promising approach to recycle and leverage nutrients more efficiently, mitigating the nutrient pollution of waterbodies (**li2021toward**). However, the technologies that can be implemented at CAFOs differ widely in aspects such as phosphorus recovery performance, final products obtained, capital expenses, and operational costs. Additionally, different levels of environmental vulnerability to eutrophication may require the use of different P recovery processes, searching for the most effective balance between P recovery efficiency and cost. Previous efforts for the technical evaluation of different phosphorus recovery technology have been performed, resulting in processes with proven technical feasibility for phosphorus recovery. Particularly, there exists a considerable body of literature on the production of struvite (**muhmood2019formation**). Other mature processes for the recovery of phosphorus are the formation of calcium precipitates (**berg2006phosphorus**), and systems based on physical separations (**church_novel_2016**). Additionally, novel processes are currently under development, such as membrane separation processes (**li2020application**), microalgae-based processes (**robles2020new**), adsorption using biochar (**wang2020phosphorus**), and electrochemical processes (**belarbi2020bench**). Moreover, a decision-making framework has been developed for the selection and implementation of phosphorus recovery systems in urban areas (**pearce2015phosphorus**). However, to the best of the authors knowledge, there are no specific frameworks to study the implementation of phosphorus recovery systems at livestock facilities considering GIS environmental and techno-economic dimensions.

In this work, we propose a novel framework, COW2NUTRIENT (Cattle Organic Waste to NUTRIent and ENergy Technologies), for the assessment and selection of phosphorus recovery technologies at CAFOs based on environmental and techno-economic criteria. This framework combines eutrophication risk data at subbasin level and the techno-economic assessment of six state-of-the-art phosphorus recovery processes in a multi-criteria decision analysis (MCDA) model. This information is normalized and aggregated for the selection of the most suitable technology for each analyzed CAFO. The goal is to develop a flexible framework able to balance the operating cost of the systems and P recovery efficiency as a function of the environmental vulnerability to eutrophication of each region. The minimization of operating costs is prioritized in regions with low eutrophication risk, while the efficiency of P recovery is the most relevant criteria in regions affected by nutrient pollution. Also, COW2NUTRIENT aims to provide a useful framework for designing and evaluating effective GIS-based incentives and regulatory policies to control and mitigate nutrient pollution of waterbodies. The practicability of the proposed framework is assessed by studying and designing the implementation of P recovery systems at 2,217 current livestock facilities in the Great Lakes area.

4.2 METHODS

COW2NUTRIENT framework is comprised by three models, i.e. environmental geographic information, techno-economic, and multi-criteria decision analysis models, in order to integrate the geographic data on vulnerability to nutrient pollution, and the technical and economic information of the nutrient recovery systems through an MCDA model, as shown in Figure 4.1. First, the geographic location of the individual facilities (longitude and latitude) is supplied to the environmental GIS model to determine the vulnerability level to nutrient pollution of the region where the studied CAFOs are located. Secondly, data regarding the number and type of animals at the facility (i.e., beef and dairy cattle, adult animals, heifers, and calves) are entered into the techno-economic model to capture the characteristics of the livestock facility evaluated. Data reported by the US Department of Agriculture were considered for manure generation ratios (**Kellog2010**) and composition (**USDAHandbook**). These values are collected in Table 3S of the Supplementary Material. In addition, economic data are fed into the techno-economic model for economic performance evaluation purposes, including the value of incentives received for phosphorus recovery (in the form of P credits), and for the generation of bio-based methane or electricity (in form of Renewable Energy Certificate (REC) and Renewable Identification Number (RIN) respectively). The output data from the techno-economic and environmental geographic information models are imported in the MCDA model. In this module, the data is normalized and aggregated, returning a composite index for each technology. This composite index is used to score and rank the nutrient recovery systems based on their performance. All models have been developed using Python (**Python**).

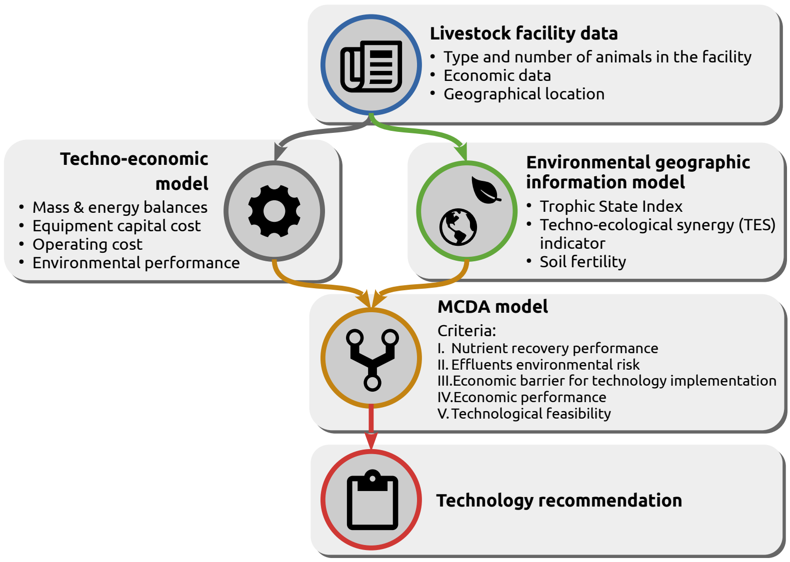


Figure 4.1: Structure of the COW2NUTRIENT decision support framework for the assessment and selection of phosphorus recovery systems.

4.2.1 *Environmental geographic information model*

The environmental vulnerability to nutrient pollution of the area where the livestock facilities are located determines the preference (i.e., ranks the importance) of each criterion. Three indicators are used to evaluate the eutrophication risk of each region studied at subbasin spatial resolution. The trophic state of waterbodies is evaluated through the Trophic State Index (**carlson_trophic_1977**), determining their eutrophication level. The phosphorus saturation of soils, which can result in the transport of phosphorus to waterbodies by run-off, is evaluated through Mehlich 3 phosphorus concentration (**Espinoza2006**). Finally, the balance between phosphorus releases and uptakes from anthropogenic activities is assessed through the techno-ecological synergy metric (**TESmetric**), determining if there is a net accumulation or depletion of phosphorus in a region over time. The use of these three indicators makes it possible to determine if there exist an immediate risk of eutrophication in the region studied (eutrophized waterbodies), a long-term risk (moderate value of TSI, soils saturated by phosphorus, or phosphorus releases and uptakes from anthropogenic activities unbalanced), or if there is no risk of eutrophication (phosphorus uptakes and releases are balanced). Detailed descriptions of the performed data analysis, and maps for the contiguous US are provided in Section 1 of the Supplementary Material.

4.2.1.1 *Spatial resolution*

A watershed is defined as the region draining all the streams and rainfall to a common waterbody, defining the geographic limits for the collection of runoff elements. US watersheds are designated by the US Geological Survey through the Hydrologic Unit Code (HUC) system. The HUC system divides the US into regions, subregions, basins, subbasins, watersheds, and subwatersheds. Each hydrologic unit of these six levels is identified hierarchically by a unique numeric code from 2 to 12 digits (i.e., HUC2 to HUC12). The spatial resolution of this study is the contiguous United States at the subbasin level, defined by the HUC system at 8 digits (HUC8) (**HUC8**).

4.2.1.2 *Trophic State Index*

The Trophic State Index (TSI) is a metric proposed by **carlson_trophic_1977** to determine the trophic status of waterbodies (**QAPP2012**). The TSI of a waterbody is scored in a range from 0 to 100 representing its throphic state, as shown in Table 4.1. Oligotrophic and mesotrophic states denote low and intermediate biomass productivities, while eutrophic and hypereutrophic states are referred to waterbodies with high biological productivity and frequent algal blooms. Combined data for chl-α and total phosphorus concentrations retrieved from the National Lakes Assessments conducted by the US EPA in 2007 and 2012 (**NLA2012**; **NLA2007**) is used to determine the Trophic State Index of lentic waters in the contiguous US. No TSI values were assigned to the watersheds without reported data. Correlations to estimate the TSI from chlorophyll-α and total phosphorus concentrations are collected in Section 1 of Supplementary Material.

Table 4.1: Relation between TSI value and trophic class.

TSI	<40	40-50	50-70	>70
Trophic Class	Oligotrophic	Mesotrophic	Eutrophic	Hypereutrophic

4.2.1.3 *Techno-ecological synergy sustainability metric*

The techno-ecological synergy sustainability metric (TES) is an indicator proposed by **TESmetric** to evaluate the fraction of net anthropogenic phosphorus releases, Eq. 4.1.

$$V_x = \frac{(U_x - E_x)}{E_x} \tag{4.1}$$

A negative value for TES indicator (V_x) indicates that the releases (E_x) are larger than the uptake capacity of the evaluated system, (U_x), and thus impacting in the ecosystems; while positive values reflects that the releases can be absorbed by the system without any harm.

Phosphorus releases from agricultural activities have been estimated from data reported by the Nutrient Use Geographic Information System project. Since this work is limited to the assessment of agricultural phosphorus releases, other possible sources of phosphorus releases are not considered. Further information about the methodology used for the estimation of human-based phosphorus releases can be found in **NuGIS**. Anthropogenic phosphorus uptakes are those due to the crops grown in each watershed, including corn, soybeans, small grains, cotton, rice, vegetables, orchards, greenhouse and other crops (i.e., fruits, sugar crops, and oil crops). The estimation of the phosphorus uptakes is performed considering the different phosphorus requirements and yield rates of each crop, as well as the land cover and the crops distribution in each watershed. Data retrieved from **2017CensusofAgriculture**, **USDAHandbook**, and **EnviroAtlas** is used for this purpose.

4.2.1.4 *Phosphorus saturation of soils*

Phosphorus concentration in soil is used for the evaluation of the phosphorus legacy that is continuously built up in soils, providing a metric of soil quality. However, only a fraction of phosphorus is available for plants. To measure this phosphorus fraction available for plants, several standardized phosphorus soil tests have been proposed, including Olsen, Bray 1, and Mehlich 3 tests. Among them, Mehlich 3 (M3P) has been selected as a measure of the concentration of P in soils since it is a widely used metric, and it is the P soil test least affected by changes in soil pH. To estimate the fraction of phosphorus available for plants from total phosphorus concentration data, a correlation developed by **AllenMallarino2006** has been used, Eq. 4.2. It must be noted that this correlation has been developed for agricultural soils in Iowa, but due to the lack of studies in this topic, it has been used for soils throughout the contiguous US. Therefore, it must be considered as an exploratory effort to determine the phosphorus saturation in the US soils. Data reported by **SoilsUSGS** is used to evaluate the concentration of total phosphorus along the contiguous US.

$$\text{M3P (\% over TP)} = \frac{4.698 \cdot 10^{-1}}{1 + \left(\text{TotalP (mg/kg)} \cdot 1.336 \cdot 10^{-3}\right)^{-2.148}} \quad (4.2)$$

The relationship between M3P test value and the quality of soil is shown in Table 4.2. Soil fertility levels below optimum indicate that nutrient supplementation is needed to enhance the yield of crops, optimum values indicates that no nutrient supplementation is needed, and excessive soil fertility level indicate over-saturation of phosphorus in soil that can reach waterbodies by runoff (**Espinoza2006**).

Table 4.2: Relationship between Mehlich 3 phosphorus and soil fertility level (**Espinoza2006**).

Soil Fertility Level	M3P soil phosphorus concentration (ppm)
Very Low	<16
Low	16-25
Medium	26-35
Optimum	36-50
Excessive	>50

4.2.2 *Techno-economic model*

COW2NUTRIENT framework evaluates all the stages involved in the processing of manure for P recovery, from organic waste collection to the recovery of nutrients and other by-products such as electricity or biomethane, as represented in Fig 4.2. In addition to the assessment of nutrient recovery systems, the framework is flexible to include anaerobic digestion, and the subsequent biogas valorization, for the production of methane or electricity. The techno-economic model is based on mass balances, thermodynamics, and chemical equilibria for each possible stage of the manure treatment process, i.e. manure conditioning, anaerobic digestion, biogas purification, biogas valorization, and phosphorus recovery. Preliminary design and sizing of equipment is performed to estimate the capital and operating expenses when no specific costs data are available. A detailed description of equipment design and sizing, as well as the correlations used for costs estimation, can be found in Section 2 of the Supplementary Material.

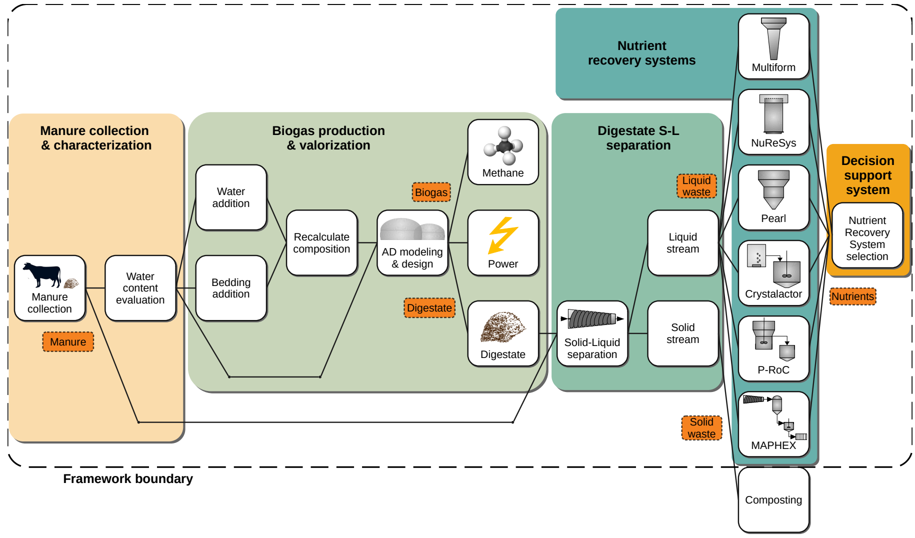


Figure 4.2: Process flowsheet for manure management and phosphorus recovery stages included in COW2NUTRIENT.

4.2.2.1 *Manure conditioning*

It is considered that the collection of manure does not involve any cost, since CAFOs have manure collection systems already installed. All manure produced is assumed to be collected. If the anaerobic digestion (AD) stage is implemented, a preconditioning stage is considered to adjust the water content of the waste. US EPA determines that the content of total solids in manure should be less than 15% (**AgSTARHandbook**), as shown in Figure 6S of the Supplementary Material. Therefore, additional water may be added to reduce the solids content in manure before the AD stage.

4.2.2.2 *Anaerobic digestion*

Anaerobic digestion is a microbiological process that breaks down organic matter in the absence of oxygen. It involves four stages, hydrolysis, acidogenesis, acetogenesis, and methanogenesis; producing a mixture of gases mainly composed of methane and carbon dioxide (biogas), and a decomposed organic substrate (digestate). The model of the anaerobic digester is formulated through the mass balances of the species involved in the production of biogas and digestate. A detailed description of the digester modeling can be found in **Leon**. As a result of the AD process, a fraction of organic phosphorus and nitrogen are transformed in their inorganic forms. To evaluate the amount of organic nutrients transformed into inorganic phosphorus and nitrogen, data available in literature was considered, resulting in an increase of 24% and 16% over the original inorganic ammonia and phosphate respectively, as shown in Table 5S of the Supplementary Material. Correlations to estimate the capital cost and operating and management costs (O&M) as a function of the animal population of CAFOs were developed using data from the US EPA AgSTAR program (**AgSTAR2003**) and the USDA (**USDA_OM**) respectively. We refer the reader to the Supplementary Material for further information.

4.2.2.3 *Biogas purification*

Before transforming biogas into marketable products, a purification stage has to be carried out to remove H_2S, H_2O, and NH_3. The removal of H_2S is performed in a bed of ferric oxide through the production of Fe_2S_3 operating at a temperature range of 25-50°C. The bed regeneration is carried out using oxygen to produce elemental sulfur and ferric oxide (Fe_2O_3). Water and ammonia are adsorbed using a pressure swing adsorption system (PSA) with zeolite 5A as adsorbent material, operating at low temperature (25°C) and moderate pressure (4.5 bar). The assumed recovery for NH_3 and H_2O is 100%. For further details about the modeling of the biogas purification stage, we refer the reader to previous works (**Leon**; **MartinHernandez**).

4.2.2.4 *Biogas valorization*

Two final added value products have been considered, methane and electricity, since they can be obtained through relatively simple processes and there exists developed markets for them.

METHANE PRODUCTION The process considered for methane production is the removal of CO_2 using a PSA system with a bed of zeolite 5A, since this process was demonstrated as the optimal biogas upgrading process by **MartinHernandez2020**, where further details about the modeling of the PSA system can be found.

ELECTRICITY PRODUCTION Electricity is produced from biogas through a gas turbine. A Brayton cycle consisting of double-stage compression system, one for the air stream and one for the biogas stream, is considered. Polytropic compression is assumed, with a polytropic index of 1.4 and an efficiency of 85% (**moran2010fundamentals**). The adiabatic combustion of methane contained in the biogas is assumed, with a pre-heating of the biogas-air mixture, considering the combustion chamber as an adiabatic furnace. An air excess of 20% with respect to the stoichiometric needs, and

100% conversion of the reaction are assumed. Further details for electricity production can be found in **MartinHernandez**.

4.2.2.5 *Solid-liquid separation*

Nutrients contained in organic waste (manure or digestate, depending on whether AD is carried out or not) are present in both organic and inorganic forms. Organic nutrients are chemically bonded to carbon, and they have to be converted into their inorganic forms through a mineralization process to be available for the vegetation to grow. Organic nutrients are mainly contained in the solid phase of organic waste. Inorganic nutrients are water soluble, and they are mostly present in the liquid phase, or bounded to soluble minerals. They are immediately available to plants, including algae involved during the occurrence of HABs. To recover the inorganic fraction of nutrients, a solid-liquid separation stage is implemented, keeping the inorganic nutrients in the liquid stage, which will be further processed, and the organic nutrients in the solid phased, which can be composted to mineralize nitrogen and phosphorus and be further used as fertilizers. The study of organic waste composting is out of the scope of this work.

Based on the evaluation reported by **MollerSLsep**, a screw press is the technology selected to carry out the solid-liquid separation stage since it is the most cost-efficient equipment. The partition coefficients for the different components are shown in Table 6S of the Supplementary Material. Assuming the discretization of units due to the commercial sizes available, the investment and operating costs for the screw press equipment are presented in Figure 9S of the Supplementary Material.

4.2.2.6 *Phosphorus recovery*

The technologies to recover inorganic phosphorus can be classified in three categories: struvite-based phosphorus recovery, calcium precipitates-based phosphorus recovery, and physical separation systems. Table 4.3 shows the classification and characteristics of the evaluated technologies. Regarding struvite-based systems, the formation of struvite has been widely described in the literature, mainly focused on phosphorus recovery from wastewater (**rahaman_modeling_2014**; **Battistoni**). However, cattle organic waste shows some characteristics that hinder struvite formation, including high ionic strength, which reduces the effective concentration of ions; and the presence of calcium ions competing for phosphate ions (**Yan2016**), which inhibits a selective recovery by phosphorus precipitation. The high variability in the manure composition, as a function of the geographic area, the animal feed, etc., represents an additional challenge for nutrient recovery (**Tao**). Therefore, specific correlations for livestock waste to estimate the molar fraction of PO_4^{3-} and Ca^{2+} recovered as struvite as a function of the amount of calcium contained in the waste were developed in a previous work (**MartinStruvite**).

Among the different products obtained by the different processes, only struvite generates income. Calcium precipitates lacks of a well-established market as fertilizer, and therefore no sales of this product are considered. MAPHEX produces an organic solid rich in nutrients, but with a lower nutrient density compared with struvite, hindering transportation of this product and decreasing its market value. Therefore, we have assumed that no income is obtained from this product. Nevertheless, the recovered products allow phosphorus distribution from CAFO releases to phosphorus-deficient areas.

All technologies considered are at or near commercial stage. We note that, for all the technologies evaluated, the installation of several P recovery units in parallel arrangement is considered if the amount of waste to be processed exceeds the treatment capacity of the system. The description of the processes, and the correlations used to estimate the struvite formed, equipment cost, and operating costs are collected in the Section 2.2.4 of the Supplementary Material.

4.2.2.7 *Incentives for the installation of nutrient recovery systems*

COW2NUTRIENT can evaluate the effect of different kinds of incentives on the economic performance of the nutrient recovery systems. These incentives can be received as a result of the recovery of phosphorus, in the form of P-credits, or for the generation of electricity or biomethane, in form of Renewable Energy Certificates (REC) and Renewable Identification Numbers (RIN) respectively. Renewable Energy Credits are a mechanism implemented in the US which guarantees that energy is generated from renewable sources, providing a system for trading produced renewable electricity. Each produced renewable megawatt-hour generates one REC, that can be sold separately from the electricity commodity itself and can be used to meet regulatory requirements by generators, trades, or end-users. On the other hand, RINs are identification numbers assigned to batches of biofuel, allowing their tracking through the production, purchase, and final usage. The allocation of RINs is associated with the allocation of incentives for the generation bio-fuels. The considered values for the different incentives are listed in Table 4S of the Supplementary Material.

Table 4.3: Description of phosphorus recovery technologies systems by COW2NUTRIENT framework. $x_{Ca^{2+}:PO_4^{3-}}$ refers to the Ca^{2+}/PO_4^{3-} molar ratio. n_i denotes the number of units of the technology i installed.

Technology	Company	Technology type	Technology readiness level	Phosphorus recovery efficiency (%)	Treatment capacity $\left(\frac{kg_{P\text{-}PO_4}}{day \cdot unit}\right)$	CAPEX $\left(\frac{MM\ USD}{unit}\right)$	OPEX $\left(\frac{USD}{kg_{P\text{-}PO_4}}\right)$	Reference
Multiform	Multiform Harvest	Struvite-based	9	$\frac{0.798 \cdot 100}{1+\left(x_{Ca^{2+}:PO_4^{3-}} \cdot 0.576\right)^{2.113}}$	38.5	1.1	15.42	1
Crystalactor	Royal Haskoning DHV	Struvite-based	9	$\frac{0.798 \cdot 100}{1+\left(x_{Ca^{2+}:PO_4^{3-}} \cdot 0.576\right)^{2.113}}$	137.7	$2.3 + 0.71 \cdot n_{\text{Crystalactor}}$	2.12	2
NuReSys	Nutrient Recovery Systems	Struvite-based	9	$\frac{0.798 \cdot 100}{1+\left(x_{Ca^{2+}:PO_4^{3-}} \cdot 0.576\right)^{2.113}}$	204.0	1.38	6.22	1
Pearl 500	Ostara	Struvite-based	9	$\frac{0.798 \cdot 100}{1+\left(x_{Ca^{2+}:PO_4^{3-}} \cdot 0.576\right)^{2.113}}$	65.0	2.3	7.54	3
Pearl 2K	Ostara	Struvite-based	9	$\frac{0.798 \cdot 100}{1+\left(x_{Ca^{2+}:PO_4^{3-}} \cdot 0.576\right)^{2.113}}$	250.0	3.1	7.54	1
Pearl 10K	Ostara	Struvite-based	9	$\frac{0.798 \cdot 100}{1+\left(x_{Ca^{2+}:PO_4^{3-}} \cdot 0.576\right)^{2.113}}$	1250.0	10.0	7.54	4
P-RoC	Karlsruhe Institute of Technology	Calcium precipitates-based	6	60	24.3	Tailored design based on waste flow processed. See Section 2.2.4.4 of Supplementary Material.	23.22 - 167.8	5
MAPHEX	University of Pennsylvania and USDA	Modular phases separation system	7	90	18.5	0.3	110.8	6, 7

1: **Pearl2Kcost2**
2: **egle_phosphorus_2016**
3: **Pearl500cost1**
4: **Pearl10Kcost1**
5: **ehbrecht_p-recovery_2011**
6: **church_novel_2016**
7: **church_versatility_2018**

4.2.3 *Multi-criteria decision model*

The determination of the most suitable nutrient management process is not a trivial procedure since multiple criteria play a critical role at the decision-making stage. COW2NUTRIENT performs the selection of P recovery technologies considering information concerning environmental, economic, and technology readiness dimensions. The integration of these dimensions is justified by the need to find the most suitable system for each CAFO by balancing operating cost and efficiency in the mitigation of nutrient pollution according to the local environmental vulnerability to eutrophication. Finally, the technical maturity of each system is also considered to assess the development level of the different processes. Therefore, a multi-criteria decision analysis (MCDA) model was developed to address the selection of the most suitable phosphorus recovery systems for each studied CAFO. The workflow of the MCDA model is summarized in Figure 4.3.

Five criteria are combined in a composite index for the assessment of the environmental, economic, and technology maturity dimensions of the different technologies. Two environmental criteria are studied to assess the performance of the different technologies to mitigate phosphorus releases from CAFOs, i.e., the fraction of phosphorus recovered, and the potential environmental threat for the local ecosystem of the effluents containing the non-recovered phosphorus evaluated through the eutrophication potential of the effluents. The economic aspect is considered by means of two criteria, the economic barrier for the implementation of P recovery processes, measured in terms of capital cost, and the overall economic performance of the systems, which is evaluated through the net present value (NPV) (**sinnott2014chemical**). Finally, the technological maturity of the different technologies is considered though the technology readiness level (TRL) index. The construction of a composite index integrating these criteria is composed of three steps: criteria normalization, weighting, and aggregation (**MarcoCinelli2020**).

4.2.3.1 *Data normalization*

Since each criteria has a different range of potential values, they must be normalized to a common scale to allow each criteria to be compared with the others. However, the composite index can be affected by the normalization technique used. In order to study the robustness of the composite index obtained, and to address the uncertainty originated by data normalization, normalized data using standardization, min-max, and target normalization methods is calculated (**HandbookCompositeIndicators**).

Table 4.4: Criteria preference as a function of the GIS-based environmental indicators for nutrient pollution.

Local environmental indicators values	Criteria ranking	Description
Condition 1: TES > TSI and TES > Soil fertility Condition 2: TES = Unbalanced	TRL > NPV > Capital cost > TP recovered > Eutrophication potential	Unbalanced phosphorus releases but no immediate threat to soil and water bodies. Prevalence of economic criteria for nutrient recovery system selection.
Condition 1: TSI $\geq$ TES or TSI $\geq$ Soil fertility Condition 2: TSI = Eutrophic or Hypereutrophic	TRL > Eutrophication potential > NPV > TP recovered > Capital cost	High Trophic State Index. Inmmediate environmental risk due to potential algal blooms. Prevalence of environmental criteria for nutrient recovery system selection.
Condition 1: Soil fertility $\geq$ TES and Soil fertility > TSI Condition 2: Soil fertility = Excessive	TRL > TP recovered > NPV > Eutrophication potential > Capital cost	Excessive P in soil. Inmmediate environmental risk due to potential P runoff. Prevalence of environmental criteria for nutrient recovery system selection.
Condition: TES $\neq$ Saturated and TSI $\neq$ Eutrophic or Hypereutrophic and Soil fertility $\neq$ Excessive	TRL > NPV > Capital cost > TP recovered > Eutrophication potential	No environmental risk. Prevalence of economic criteria for nutrient recovery system selection.

TRL: Technology Readiness Level
TSI: Trophic State Index
TES: Techno-Ecological Synergy sustainability metric
NPV: Net Present Value
TP: Total Phosphorus

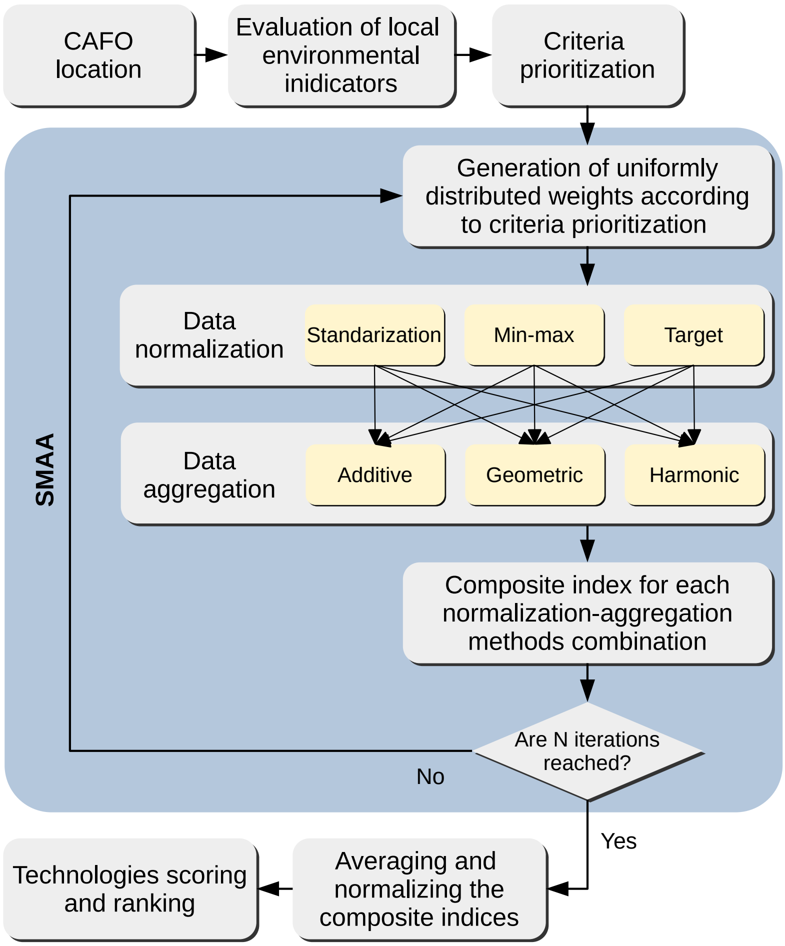


Figure 4.3: Flowsheet for the MCDA model.

4.2.3.2 *Criteria weighting*

The normalized criteria are weighted to set the relative importance of each criterion, prioritizing some criteria over others. This is needed in order to obtain a flexible decision method able to balance the operating cost of the systems and the P recovery efficiency as a function of the environmental vulnerability to eutrophication of each region. The minimization of the operating costs is prioritized in regions with low eutrophication risk, while the efficiency of P recovery is more relevant in regions affected by nutrient pollution. Therefore, the criteria are dynamically weighted according to the values of TSI, TES and Mehlich 3 phosphorus concentration in each region studied. The preference of criteria as a function of the environmental vulnerability to eutrophication is shown in Table 4.4. On the one hand, if there is immediate environmental risk by nutrient pollution (i.e., high values for TSI or soil fertility), phosphorus recovery efficiency is prioritized over economic performance. Conversely, if there is environmental risk in the long run due to the unbalance between anthropogenic phosphorus releases and uptakes (negative value of TES indicator), or there is no potential environmental risk, the economic performance is prioritized over the phosphorus recovery efficiency. Finally, since the objective of this framework is to select P recovery systems that are feasible to install and operate in CAFOs, the TRL index is set as the criteria with highest preference in all cases in order to minimize the risk of selecting non-full-scale processes. As a result, the selection of processes with low TRL will be hampered unless they have good economic or environmental performance.

The procedure described above sets the prioritization of criteria, i.e., they can be sorted in order of importance. However, it does not provide an specific value for the weights, which values are unknown. In order to avoid the risk of biasing the decision-making procedure setting arbitrary values for the weights, a stochastic multi-criteria acceptability analysis (SMAA) is used to explore the weights space (**tervonen_implementing_2007**). Through this approach, the feasible space of each weight (i.e., the space delimited by the previous and the subsequent weights) is explored through the Monte Carlo method, retrieving a set of weights for all criteria according to the assigned order. The SMAA is formulated by defining the set of n weights (ω) as a non-negative set which elements must sum 1, as shown in Eqs. 4.3 and 4.4.

$$\omega_j \geq 0 \; \forall \; j \; \in \; n \tag{4.3}$$

$$\sum_{j=1}^{n} \omega_j = 1 \tag{4.4}$$

$$\omega_{j1} \geq \omega_{j2} \geq ... \geq \omega_{jn} \tag{4.5}$$

The preference information of the criteria, defined through the ranking of the criteria shown in Table 4.4, is expressed as a sequence of inequality constraints, Eq. 4.5. A detailed description of the SMAA method can be found in **tervonen_implementing_2007**. A number of Monte-Carlo simulations (N) of 100 is assumed as a trade-off between computational cost and MCDA model performance.

4.2.3.3 *Criteria aggregation*

The aggregation stage merges the weighted criteria, resulting in the composite index. Similarly to the normalization stage, different aggregation methods are evaluated to improve the robustness of the solutions retrieved by the framework. Different aggregation schemes denote different degrees of compensability between indicators, i.e. a deficit in one criteria can be fully, partially, or not compensated by a surplus in other criteria (**MarcoCinelli2020**). Three aggregation functions are evaluated including full compensation (additive aggregation) and partial compensation schemes (geometric and harmonic aggregation methods). Nine composite indexes are obtained for each P recovery technology combining normalization and aggregation techniques, as shown in Figure 4.3. Finally, the composites indexes are normalized in a range from 0 to 1 and ranked to determine the most suitable P recovery process for the CAFO under study.

4.2.4 *Framework limitations*

The main limitations of the proposed framework lie in the uncertainty of the input data. On the one hand, since the data regarding the animal number, type of animals, and location of CAFOs are reported by the state environmental protection agencies of each state, they are considered reliable. On the other hand, to estimate the local vulnerability to phosphorus pollution throughout the contiguous US, HUC8 spatial resolution has been chosen as a trade-off solution between spatial accuracy and data uncertainty. However, more accurate results can be obtained if reliable data for phosphorus level in soils, fertilizer application rates, etc. are available for higher spatial resolution. Particularly, further studies for developing more accurate correlations to estimate the fraction of phosphorus available to plants based on soil type and climate conditions in each region would improve the accuracy of the assessment of local risk to phosphorus pollution. Additionally, since the proposed framework is focused on phosphorus recovery for freshwater nutrient pollution prevention and control, the recovery of other resources contained in livestock manure (such as organic carbon and nitrogen) is not considered in this study.

4.2.5 *Case study*

4.2.5.1 *Study region*

The Great Lakes area, located in North America, is selected in order to demonstrate the implementation of nutrient management systems at

CAFOs using the COW2NUTRIENT framework. This region is selected because its high concentration of CAFO facilities, resulting in significant nutrient releases that contribute to frequent HABs and eutrophication episodes, as well as to the nutrient legacy accumulated over time (**sayers2019satellite**; **han2012historical**). The evaluation and implementation of phosphorus recovery systems at CAFOs already in operation at the US states of Pennsylvania (**Pennsylvania_CAFOS**), Ohio (**Ohio_CAFOS**), Indiana (**Indiana_CAFOS**), Michigan (**Michigan_CAFOS**), Wisconsin (**Wisconsin_CAFOS**), and Minnesota (**Minnesota_CAFOS**) are performed using the criteria prioritization based on the GIS indicators describing the environmental impact of nutrient pollution shown in Table 4.4. The states of Illinois and New York, and the Canadian province of Ontario, which are also part of the Great Lakes area, are not included due to the unavailability of reliable information about their CAFOs. A description of the studied states listing the animal units, annual manure generation, and annual phosphorus releases by the year 2019, disaggregated for dairy and beef cattle, is collected in Table 10S of the Supplementary Material.

It should be noted that, accordingly to the US regulatory definition of CAFOs, only intensive livestock facilities with 300 animal units or more are considered in this study (**CAFO_definition**), resulting in the evaluation of 2,217 CAFOs. An animal unit is defined as an animal equivalent of 1,000 pounds (453.6 kg) live weight (**animal_unit_definition**). Animal units is used as a unit to measure the size of CAFOs due to the presence of different types of animals in the CAFOs, i.e. beef or dairy cows, and animals of different age, including heifers, calves, and adult animals. Different types of animals result in different manure generation rates and composition. Therefore, the different types of animals within each studied CAFO are normalized using the definition of animal units to estimate the amount and composition of the manure generated.

4.2.5.2 *Scenarios description*

Two scenarios have been evaluated, the deployment of only phosphorus recovery systems, and the integration of these processes with AD and electricity production processes. Incentives for the recovery of phosphorus based on the work of **sampat_economic_2018** are considered, assuming a phosphorus credit value of 22 USD/$kg_{\text{P recovered}}$ for both scenarios. We note that this value is significantly lower than the economic impact of P release from livestock waste, valued in 74.5 USD/$kg_{\text{P released}}$ (**sampat2021valuing**). Additionally, in the scenario considering the production biogas-based electricity, a value of Renewable Energy Certificates (fixed electricity selling price) of 60 USD per MWh generated is assumed. Finally, a discount rate of 7% is considered in both scenarios.

4.3 RESULTS

4.3.1 *Implementation of phosphorus recovery systems in the Great Lakes area*

Table 4.5 summarizes the results of the phosphorus recovery process selection in the Great Lakes area. It can be observed that only three out of the six commercial processes evaluated are selected to be installed. All selected processes recover P in the form of struvite, which is a valued product that can be sold, generating income. Although the Ostara Pearl process also produces struvite, it results in larger operating costs than the technologies selected. Conversely, P-RoC recovers phosphorus in the form of calcium-based precipitates. This product lacks a well-established market, and therefore it does not generate income. In addition, P-RoC is the technology with the lowest TRL, which hampers the selection of this process. The selection of modular phosphorus recovery systems, such as MAPHEX, which due to economies of scale are especially suitable for small livestock facilities, is largely prevented by the absence of small-scale CAFOs. Therefore, a sub-set of three technologies is obtained. Therefore, it can be concluded that the selection of this pool of three technologies amongst the six systems evaluated is mainly driven by economic factors. Additionally, the low TRL of P-RoC also hampers the selection of this process.

The selection of the most suitable technology for each studied CAFO among the sub-set comprised by Multiform, Nuresys, and Crystalactor systems is based on the CAFO scale and local eutrophication risk, as it is discussed in the following sections.

4.3.1.1 *Effect of CAFOs scale on selecting P recovery systems*

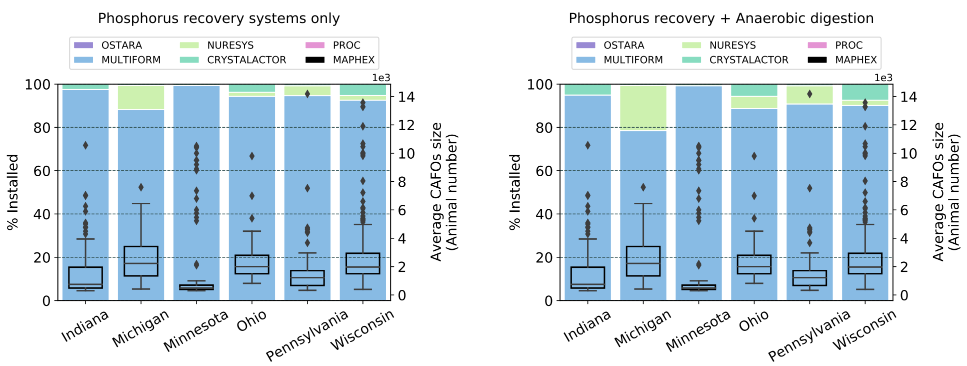
A relationship between CAFOs size and the selected technologies can be observed in Table 4.5. This relationship is also observed in Figures 4.4 and 4.5. Multiform is the predominant phosphorus recovery process. Furthermore, we observe that in those states with smaller CAFOs (Minnesota and Indiana) the selection of Multiform is more predominant than in states with larger CAFOs. On the contrary, in the states with large CAFOs or with outliers representing large facilities, (such as Ohio and Wisconsin) Crystalactor is selected for some facilities. Additionally, NuReSys is a technology also selected for medium-size CAFOs.

Table 4.5: Distribution and characteristics studied CAFOs, and phosphorus recovery processes selected. Only selected technologies are included in the table.

State	CAFO average size (animal units)	Number of CAFOs	Manure generated (ton/year)	P recovered (ton/year, (%))	Number of phosphorus recovery systems installed					
					Multiform		NuReSys		Crystalactor	
					S1	S2	S1	S2	S1	S2
Indiana	1,574.41	119	$2.48 \cdot 10^6$	1558.8 (78.7)	116	113	0	0	3	6
Michigan	2,461.52	144	$4.76 \cdot 10^6$	3004.4 (79.0)	127	113	16	30	1	1
Minnesota	634.23	1,487	$1.13 \cdot 10^7$	6938.1 (76.9)	1,477	1,476	0	0	10	11
Ohio	2,415.24	53	$1.68 \cdot 10^6$	1055.8 (78.6)	50	47	1	3	2	3
Pennsylvania	1,495.94	131	$2.59 \cdot 10^6$	1633.2 (78.9)	124	119	6	11	1	1
Wisconsin	2,628.19	283	$1.02 \cdot 10^7$	6510.5 (79.4)	262	255	6	7	15	21

S1: Phosphorus recovery systems only.
S2: Phosphorus recovery systems coupled with AD and electricity production.

The integration of biogas production and upgrading affects the selection of P recovery processes as a consequence of the high investment expenditures associated to the installation of AD processes. These large costs blur the capital investment differences between different P recovery processes. As a result, the MDCA model promotes the implementation of technologies with better long-term economic performance (lower operating costs), such as NuReSys and Crystalactor, in spite of the fact that they involve larger investments costs than other technologies like Multiform, as shown in Figure 4.4b.



(a) Phosphorus recovery systems only.

(b) Phosphorus recovery systems coupled with AD and electricity production.

Figure 4.4: Distribution of the phosphorus recovery systems selected for the CAFOs in the Great Lakes area. The boxplots represent the distribution of CAFO sizes in each studied state.

Based on the data illustrated in Figures 4.5 to 4.7, a preliminary screening of P recovery systems can be performed based on the size of the CAFOs. If the installation of only nutrient recovery systems is considered, Multiform can be selected for CAFOs with sizes up to 5,000 animal units, NuReSys can be selected for CAFOs with a size between 2,000 and 5,000 animal units, and Crystalactor is selected for CAFOs larger than 5,000 animal units. For the scenario integrating anaerobic digestion and phosphorus recovery processes, Multiform is mostly selected for CAFOs up to 4,000 animal units, although it is also selected in some larger CAFOs, NuReSys are mostly selected for CAFOs between 2,000 and 6,000 animal units, while the size range for the selection of Crystalactor is similar to the previous case. The operating costs are shown in Figure 4.6. It can be observed that the operating cost of Multiform is larger than NuReSys, and in turn the operating cost of this one is larger than Crystalactor, showing an opposite pattern than capital costs.

4.3.1.2 *Effect of local eutrophication risk on the selection of P recovery systems*

The results obtained reveal that CAFOs scale is the main driver for the selection of phosphorus recovery technologies. However, the role of the environmental vulnerability to eutrophication can be appreciated in those CAFOs where two different systems show similar economic performance. From the results illustrated in Figure 4.7, it can be observed that Multiform and NuReSys technologies are selected for CAFOs with similar size. However, the economic performance of the second technology is better as consequence of the lower operating expenses and larger net revenues of this technology. Although both technologies have similar phosphorus recovery yield, Multiform shows better environmental performance since the eutrophication potential of its output streams is lower than NuReSys effluents. This difference in eutrophication potential between both technologies is mainly driven by the higher nitrogen recovery of Multiform. Therefore, in those locations that are highly vulnerable to nutrient pollution, the solution proposed by the COW2NUTRIENT framework is driven more by environmental criteria than by economic criteria, resulting in the selection of the Multiform process.

4.3.2 *Economic results*

The capital expenditures (CAPEX), operating expenses (OPEX), and net revenues (difference between incomes and operating expenses) associated with the deployment of the nutrient management systems are listed per state in Table 4.6. For the scenario considering the installation of only

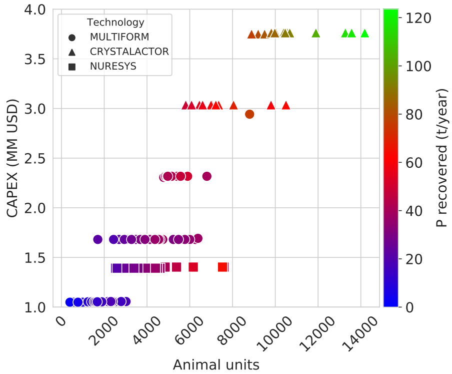
Table 4.6: Economic results per state for installing phosphorus recovery systems in the studied states of the Great Lakes area.

State	CAPEX (MM USD)		OPEX (MM USD/year)		Net revenue (MM USD/year)	
	S1	S2	S1	S2	S1	S2
Indiana	145.58	325.00	21.18	34.16	19.32	11.88
Michigan	191.09	480.19	36.74	55.92	41.00	32.15
Minnesota	1,591.40	2,866.31	140.74	251.58	39.61	-46.15
Ohio	68.30	179.29	12.95	20.32	14.46	10.80
Pennsylvania	148.16	332.03	21.46	35.03	20.82	12.95
Wisconsin	396.24	1,009.47	73.55	117.80	95.44	74.14

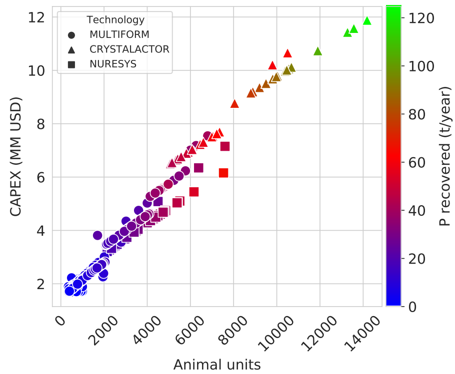
S1: Phosphorus recovery systems only.
S2: Phosphorus recovery systems coupled with AD and electricity production.

phosphorus recovery processes, the CAPEX and OPEX are 2,540.77 MM USD and 185.65 MM USD per year respectively. If the integration of biogas production and upgrading to power with phosphorus management is considered, the CAPEX and OPEX increase up to 5,192.29 MM USD and 267.51 MM USD per year respectively. It can be observed that, due to the high CAPEX of biogas production and upgrading stages, the net revenues decrease from 230.65 MM USD per year for the scenario considering only phosphorus recovery systems to 95.77 MM USD per year if the processes for phosphorus recovery and AD are combined.

Figures 4.5 and 4.6 show the evolution of CAPEX and OPEX of the P recovery technologies installed at the livestock facilities studied as a function of CAFOs scale. Figure 4.5a shows the CAPEX when the implementation of only P recovery systems is considered. We observe that CAFOs are grouped in sets selecting the same P recovery technology. This is because the manufacturers standardize the size of each P recovery technology, which in turn determines the maximum waste processing capacity of each technology (as shown in Table 4.3). This results in the use of the same P recovery equipment, and thus the same CAPEX, for all the CAFOs generating waste below the maximum processing capacity. Likewise, we note different CAPEX values for the implementation of the same P recovery technology. This is a consequence of installing of multiple in-parallel P recovery units to increase the processing capacity of such technology, since the waste generated in that CAFO exceeds its maximum processing



(a) Phosphorus recovery systems only.

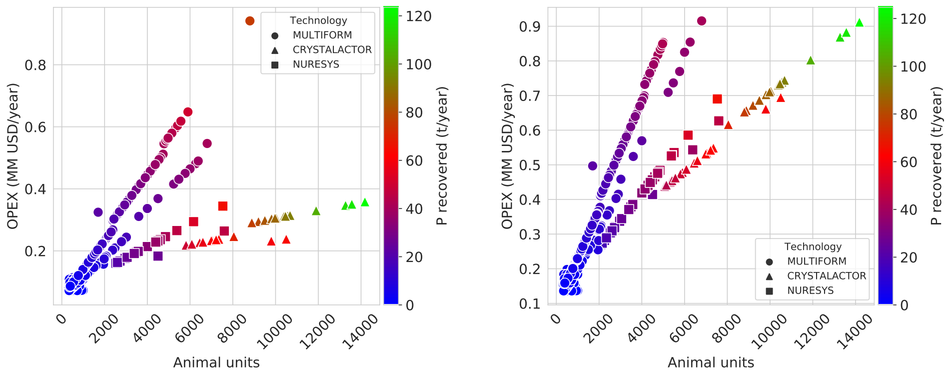


(b) Phosphorus recovery systems coupled with AD and electricity production.

Figure 4.5: Capital expenses for deploying phosphorus recovery systems in the studied CAFOs. The dots represent the P recovery technologies installed in the studied CAFOs.

capacity. It can also be appreciated that CAFOs with similar size might result in the installation of different technologies, or a different number of units of the same technology. This is because, although CAFOs can have a similar number of animal units, the type of the animals can be different, resulting in the generation of different amounts of manure. In the case of considering biogas production and upgrading, illustrated in Figure 4.5b, the required CAPEX increases significantly, blurring the differences in the capital investment between different P recovery processes observed in Figure 4.5a into the cost of the whole system. The integration of AD and electricity production also results in the increase of the OPEX, as shown in Figure 4.6.

The net revenue of the installed nutrient management systems according with the economic parameters described at the beginning of the section is shown in Figure 4.7. We observe a pattern characterized by the increase of the net revenues with the increase of CAFOs size. However, the implementation of P recovery technologies in CAFOs below 1,000 animal units, and below 2,000 animal units if biogas production and upgrading is also considered, result in economic looses. Additionally, the integration of these processes slightly decreases the net revenues of the systems installed for phosphorus recovery.



(a) Phosphorus recovery systems only.

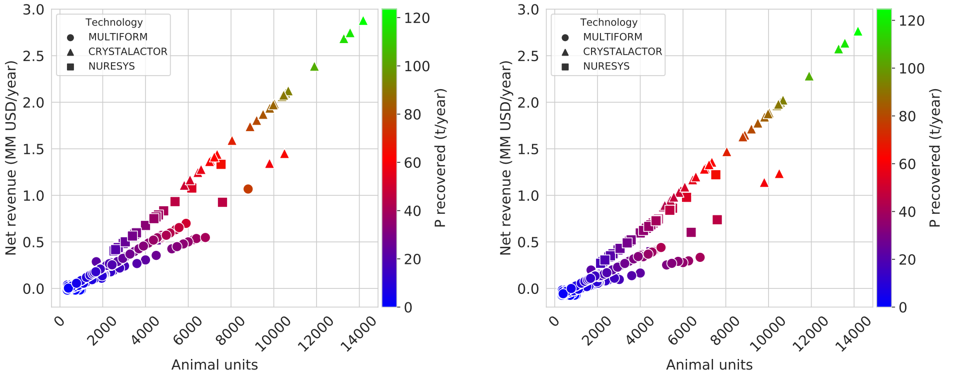
(b) Phosphorus recovery systems coupled with AD and electricity production.

Figure 4.6: Operating expenses for deploying phosphorus recovery processes in the studied CAFOs. The dots represent the P recovery technologies installed in the studied CAFOs.

4.4 DISCUSSION

4.4.1 *Economic implications*

In this work, fixed incentives for P recovery and biogas-based electricity generation have been considered as starting point to explore the effect of the application of incentives in the implementation of P recovery technologies, either standalone or integrated with biogas production and upgrading processes. The results shown in Figure 4.7 reveal the effect of the economies of scale in the net revenues from the implementation of P recovery technologies in the Great Lakes area are highly dependent on the economies of scale, i.e., the larger the amount of waste to be treated, the larger the net revenues obtained. However, while for the largest CAFOs significant profits are obtained, negative revenues (i.e., economic looses) are obtained for the smallest CAFOs, even for large P credits prices such as 22 USD/kg$_{\text{P recovered}}$. This suggests that the implementation of fixed incentives is not a fair policy, since the small CAFOs are not profitable while they increase the profits of the largest CAFOs. Therefore, alternative incentive policies must be explored. **sampat2019coordinated** studied the development of a coordinated management system for the treatment of cattle manure and P recovery. That framework captures the geographical phosphorus imbalance by proposing different prices for manure treatment that capture the regional remediation cost caused by P releases. They found that economic drivers are needed for a cost-effective recovery and redistribution of phosphorus, considering fixed incentives for P recovery



(a) Phosphorus recovery systems only.

(b) Phosphorus recovery systems coupled with anaerobic digestion and electricity production.

Figure 4.7: Net revenue from the phosphorus recovery processes selected in the studied CAFOs. The dots represent the P recovery technologies installed in the studied CAFOs.

up to 50 USD/kg$_P$ for this purpose. Therefore, further research about the effect of implementing dynamic incentives for P recovery is needed. These incentive policies can follow different schemes, such as progressive incentives for P recovery based on the amount of manure treated, or cooperative schemes where the profits from P recovery obtained by the largest livestock facilities are redistributed to the smallest CAFOs. This is a concept that has been studied for minimizing the costs of meeting greenhouse gases emission targets (**galan2018time**), and could be adopted for the reduction of P releases.

Furthermore, consideration should be given to the fair allocation of incentives in those scenarios where the available incentives budget is not enough to avoid economic looses in all CAFOs. In this regard, the fairness measure considered for budget allocation must be carefully selected among the existing schemes (**sampat2019fairness**).

4.4.2 *Phosphorus use efficiency*

Currently, manure or digestate in liquid phase is usually supplied as nutrient supplementation in croplands, or it is treated in either aerobic or anaerobic ponds. Solid phase processing is based on composting or drying. However, the high density of manure and digestate and low concentration of nutrient prevent an efficient redistribution of the phosphorus released from CAFOs to phosphorus-deficient areas (**burns2002phosphorus**). Therefore, the implementation of phosphorus recovery processes is a desirable measure for sustainable phosphorus management. We find that implementing struvite production processes considering incentives for P recovery of 22 USD/$kg_{P\ recovered}$ is economically feasible for CAFOs larger than 1,000 animal units if standalone P recovery technologies are implemented, and for CAFOs larger than 2,000 animal units if they are integrated with biogas production and upgrading processes. The requirement of large incentives to produce profit in most of the P recovery systems installed at CAFOs might raise the debate of whether it is worthwhile to implement P recovery systems; or if the economic resources should be allocated to simpler phosphorus management alternatives, such as the redistribution of either raw or pond-stored manure. In this regard, **sampat2019coordinated** studied the separation of manure in liquid and solid phases, and their further transport to demanding allocations, considering a coordinated management system in Upper Yahara watershed (Wisconsin, United States). In addition, that study considered the implementation of economic incentives from 0 to 50 USD/kg_P. However, the results showed that manure redistribution is not an economically viable technique for phosphorus recycling in this range of incentives. The main drawback of manure redistribution is the large transportation cost of both liquid and solid raw manure because of the high volume of these materials and their low phosphorus concentration. Therefore, the results reveal that on-site manure processing to generate valuable products (struvite) is more beneficial than manure redistribution.

The replacement of phosphorus from synthetic fertilizers by the recovered P, mitigating the dependency on fertilizers from non-renewable resources (phosphate rock), is an interesting alternative towards the sustainability of the agri-food sector. However, phosphorus availability for plants depends on several factors, including the P product used as fertilizer and soil pH level. Since struvite is the product recovered in all studied CAFOs, we will focus the discussion on this product. **vaneeckhaute2015efficiency** compared the bio-availability of several bio-based fertilizers, including struvite, to synthetic triple super phosphate (TSP). This study shows that P available in soil (measured as Prhizon) was a 45% higher than TSP in acidic soils (pH=5.0), but 60% lower in slightly basic soils (pH=7.9). Based on these data, one kilogram of manure processed for P recovery by struvite production can replace from $1.53 \cdot 10^{-3}$ to $3.71 \cdot 10^{-3}$ kg of TSP ($5.02 \cdot 10^{-3}$ kg of struvite are recovered per kilogram of manure processed). However, it must be noted that currently the cost of recovered P from manure (2.12-15.42 USD/$kg_{P\ recovered}$, see Table 4.3) is considerable larger than the cost of phosphorus from synthetic TSP (1.23 USD/kg_P) (**fertilizers_price**). As a result, from an economic perspective the complete substitution of phosphate rock is currently hindered by the large recovery costs, in addition to a limited availability of resources recovered from waste, and henceforth further exploration on resource recovery from different wastes is required to achieve P circularity reducing the recovery costs, and increasing the amount of phosphorus from organic waste, including but not limited to livestock manure.

4.5 CONCLUSION

We presented a framework for the techno-economic evaluation and selection of phosphorus recovery systems considering the local vulnerability to phosphorus pollution through a GIS environmental model. A multi-criteria decision analysis model is used for the comparison and section of phosphorus recovery systems based on the economic performance and technological readiness level of the processes, and the eutrophication risk of the watershed where the studied CAFOs are located. Technologies for P recovery in the form of struvite are selected in all CAFOs studied. The selection of P recovery technologies is mainly driven by economic criteria, and the effect of the economies of scale is very significant. However, environmental criteria (P recovery efficiency, eutrophication potential of process effluents) are the decision criteria at some CAFOs where different technologies show similar economic performances. The results show that a preliminary screening of P recovery systems can be performed based on the size of CAFOs. Multiform can be selected for CAFOs with sizes up to 5,000 animal units, NuReSys can be selected for CAFOs with a size between 2,000 and 5,000 animal units, and Crystalactor is selected for CAFOs larger than 5,000 animal units. The implementation of these systems in the Great Lakes area involves capital expenditures of 2.5 billion USD and operating costs of 186 million USD per year if only phosphorus recovery technologies are installed, and 5.2 billion USD and 268 million USD per year respectively if biogas production and upgrading are also considered. The implementation of fixed incentives of 22 USD/$kg_{P\ recovered}$ is considered to avoid economic looses due to P recovery costs impact in the economy of CAFOs. However, we find that that the implementation of fixed incentives is not a fair policy, since the small CAFOs are not profitable while they increase the profits of the largest CAFOs. The phosphorus recovered in the form of struvite from one kilogram of manure processed can replace from $1.53 \cdot 10^{-3}$ to $3.71 \cdot 10^{-3}$ kg of synthetic triple super phosphate, but incurring in significantly larger production costs (2.12-15.42 USD/$kg_{P\ recovered}$) than synthetic fertilizer (1.23 USD/kg_P).

As part of future work, customized incentive policies adapted to the particularities of each livestock facility can be proposed in order to optimize the allocation of limited monetary resources. Additionally, it would be interesting to analyze the potential of crop-livestock integration as an alternative for phosphorus recycling to the implementation of physicochemical P recovery processes. Another interesting research line is the integration of multiple processes in order to recover additional valuable products from organic waste (such as biochar), adapting the concept of refinery to resource recovery from organic waste.

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BIBLIOGRAPHY

Part II

NITROGEN MANAGEMENT AND RECOVERY

Part III

INTEGRATION OF ANAEROBIC DIGESTION AND NUTRIENT MANAGEMENT SYSTEMS

Part IV

APPENDIX