MODELING AND OPTIMIZATION OF SYSTEMS FOR NUTRIENT RECOVERY FROM LIVESTOCK WASTE

EDGAR MARTÍN HERNÁNDEZ

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Academic advisor: Mariano Martín Martín

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El **Dr. D. Mariano Martín Martín**, Profesor Titular de Universidad del Departamento de Ingeniería Química y Textil de la Universidad de Salamanca

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.

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ABSTRACT

Nutrient pollution of waterbodies is a major worldwide water quality problem. Excessive use and discharge of nutrients can lead to eutrophication of fresh and marine waters, resulting in environmental problems associated with algal blooms and hypoxia, public health issues related to the release of toxins, and freshwater scarcity.

Agricultural activities are one of the main contributors to anthropogenic nutrient releases. Focusing on the livestock industry, the nutrient releases, mainly phosphorus and nitrogen, result from the production of large amounts of organic waste. Particularly, the manure generated in the concentrated animal feeding operations(CAFOs) is a considerable challenge due to the high rates and spatial concentration of the organic waste generated. The abatement of nutrient releases from livestock facilities is a step to address the environmental problem of nutrient pollution.

This thesis aims at the holistic assessment of waste treatment processes and management practices for the effective recovery of nutrients from livestock waste. We have performed techno-economic assessments of phosphorus and nitrogen recovery technologies for livestock facilities to determine the systems which implementation in CAFOs is more viable, as well as the potential integration of nutrient recovery technologies with biogas production systems. Based on the information obtained in these studies, a geospatial evaluation of the impact of phosphorus recovery by deploying phosphorus recovery systems at CAFOs in the watersheds of the United States has been carried out. In addition, after establishing the most suitable type of processes for phosphorus recovery, a decision-making support tool for the selection of commercial phosphorus recovery technologies based on technical, economic, and environmental criteria of each CAFO has been developed. Finally, this tool has been used for the design and analysis of incentive policies to promote de deployment of phosphorus recovery processes at CAFOs, including the fair allocation of incentives in limited budget scenarios.

These studies are intended to contribute to the development and implementation of sustainable nutrient management strategies at livestock facilities, addressing one of the major water quality problems around the globe, and promoting the transition to a more sustainable paradigm for food production.

RESUMEN

La contaminación por nutrientes de las masas de agua es uno de los principales problemas de calidad del agua en todo el mundo. El uso excesivo de nutrientes da lugar a la eutrofización de aguas dulces y marinas, resultando en problemas medioambientales relacionados con la proliferación de algas y la hipoxia de las aguas, así como problemas de salud pública y escasez de agua potable. Las actividades agrícolas son uno de los principales contribuyentes a las emisiones antropogénicas de nutrientes. Si nos centramos en la industria ganadera, las liberaciones de nutrientes (principalmente fósforo y nitrógeno) son el resultado de la producción de grandes cantidades de residuos orgánicos. En particular, las deyecciones ganaderas provenientes de grandes instalaciones de ganadería intensiva son un reto de considerable importancia debido a las grandes cantidades de residuo generadas y su alta concentración espacial.

Esta tesis tiene como objetivo llevar a cabo una evaluación holística de los procesos de tratamiento y los procedimientos de gestión de residuos para la recuperación efectiva de nutrientes de los residuos ganaderos. Se han realizado estudios tecno-económicos de las tecnologías de recuperación de fósforo y nitrógeno con el fin de determinar los sistemas cuya implementación en las instalaciones ganaderas es más viable, así como la posible integración de estos sistemas con procesos de producción de biogás. A partir de la información obtenida en estos estudios, se ha realizado una evaluación geoespacial del impacto de la recuperación de fósforo en instalaciones ganaderas en las diferentes cuencas hidrográficas de Estados Unidos. Además, tras establecer el tipo de procesos más adecuados para la recuperación de fósforo, se ha desarrollado una herramienta de soporte a la toma de decisiones para la selección de tecnologías comerciales de recuperación de fósforo acorde a criterios técnicos, económicos y ambientales de cada instalación ganadera. Por último, esta herramienta se ha utilizado para el diseño y análisis de políticas de incentivos para promover la implementación de estos procesos en instalaciones de ganadería intensiva, incluyendo la distribución equitativa de incentivos en escenarios de presupuesto limitado.

Se pretende que estos estudios contribuyan al desarrollo y aplicación de estrategias de gestión de los nutrientes liberados por la industria ganadera, abordando uno de los principales problemas globales relacionados con la calidad del agua, y promoviendo la transición hacía un paradigma para la producción de alimentos más sostenible.

PUBLICATIONS

This thesis is based on the following publications:

Martín-Hernández, E., Sampat, A., Zavala, V., & Martín, M. (2018). Optimal integrated facility for waste processing. *Chemical Engineering Research and Design*, *131*, 160–182. doi:https://doi.org/10.1016/j.cherd.2017.11.042

Martín-Hernández, E., Guerras, L., & Martín, M. (2020). Optimal technology selection for the biogas upgrading to biomethane. *Journal of Cleaner Production*, 122032. doi:https://doi.org/10.1016/j.jclepro.2020.122032

Martín-Hernández, E., Ruiz-Mercado, G., & Martín, M. (2020). Model-driven spatial evaluation of nutrient recovery from livestock leachate for struvite production. *Journal of Environmental Management*, *271*, 110967. doi:https://doi.org/10.1016/j.jenvman.2020.110967

Martín-Hernández, E., Martín, M., & Ruiz-Mercado, G. (2021). A geospatial environmental and techno-economic framework for sustainable phosphorus management at livestock facilities. *Resources, Conservation & Recycling*, *175*, 105843. doi:https://doi.org/10.1016/j.resconrec.2021.105843

Martín-Hernández, E., Hu, Y., Zavala, V., Martín, M., & Ruiz-Mercado, G. (2022). Analysis of incentive policies for phosphorus recovery at livestock facilities in the Great Lakes area. *Resources, Conservation & Recycling*, *177*, 105973. doi:https://doi.org/10.1016/j.resconrec.2021.105973

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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 (Biraben, 1980), 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 (United Nations, Department of Economic and Social Affairs, 2019). 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 (Samreen & Kausar, 2019), the development of the Haber-Bosch process for the production of synthetic nitrogen-based fertilizers in 1913 (Smil, 1999), and the mechanization of agriculture and the development of the modern intensive farming in the XX century (Constable & Somerville, 2003; Nierenberg & Mastny, 2005).

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 (Bouwman, Beusen, & Billen, 2009). 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

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.

blooms are events resulting from the rapid increase of algae in a water system which can 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.

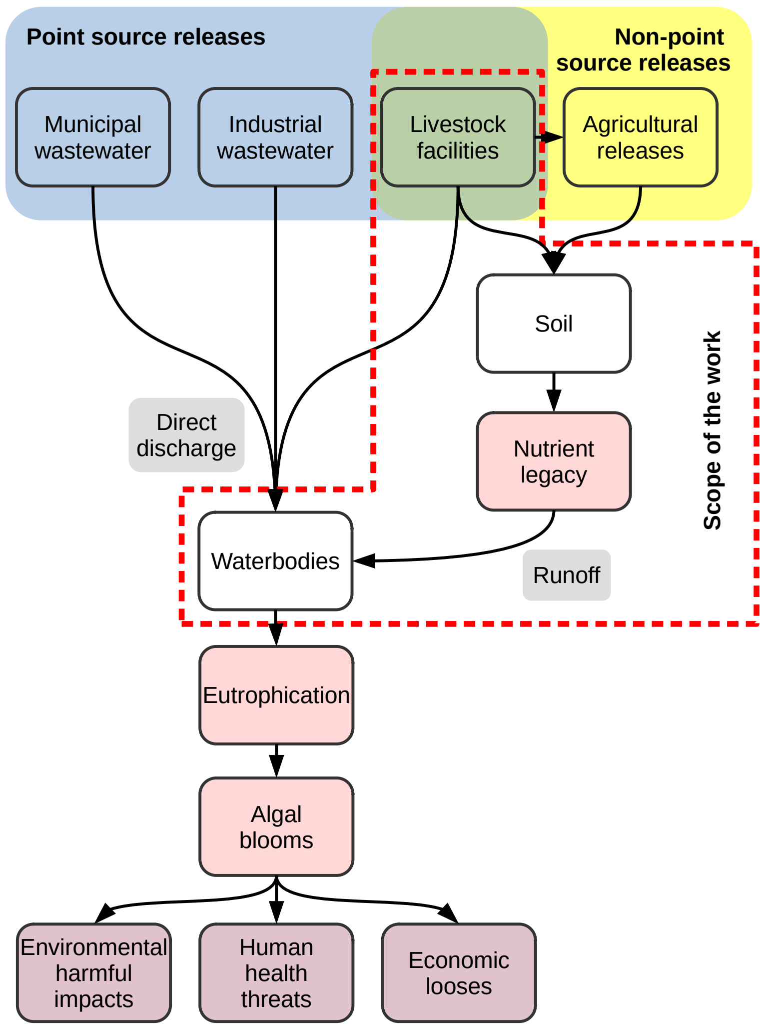

Figure 1.1: Main flows of nutrients released by anthropogenic activities.

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 (Cordell, Drangert, & White, 2009). 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 (Kellogg, Lander, Moffitt, & Gollehon, 2000). 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 (USDA, 2009). 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 (Tilley, Ulrich, Lüthi, Reymond, & Zurbrügg, 2014). 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 (Tilley et al., 2014). However, both materials, the liquid effluent obtained from the lagoons and compost, are too bulky to be economically transported to nutrient deficient locations (Burns & Moody, 2002). 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

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 (USDA, 2011). This term is used in this dissertation to denote the intensive livestock farming facilities studied.

processes for the recovery of phosphorus and nitrogen at CAFOs. At the 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) (Grizzetti et al., 2021). 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 (Amery & Schoumans, 2014).

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-Lepetit, 2011). 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 (ESSP, 2021; Comission, 2020). 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 (US EPA, 2020b). 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 (US EPA, 2020a). 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 (NACWA, 2014). 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 (CNP, 2021). Moreover, US EPA acknowledges that highly refined and primarily inorganic products (such as struvite) could be outside of the scope of these restrictions (CNP, 2021).

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 (US EPA, 2021), and BiogasAction (European Comission, 2021) and BIOGAS[3] (BIOGAS3 PROJECT, 2021) 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 scheduling

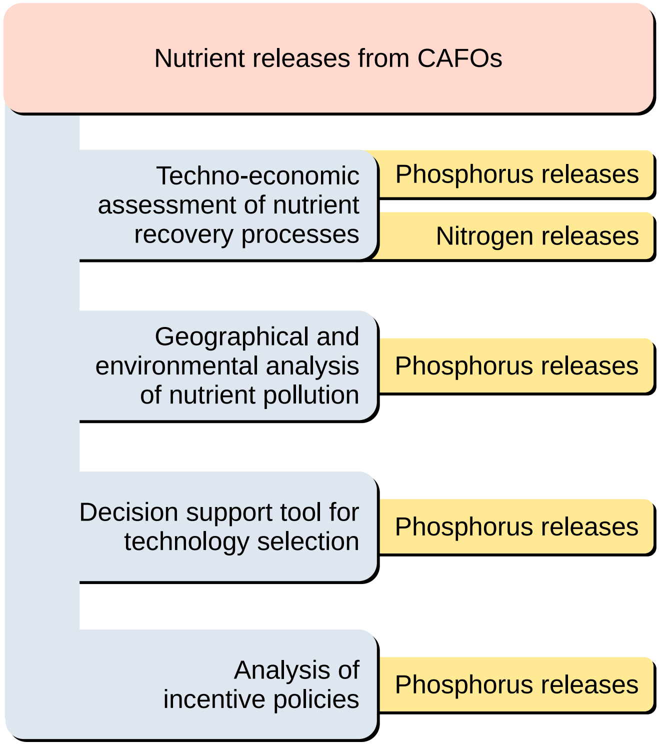

Figure 1.2: Main topics covered in this work.

and planning of the systems operations, and process control (Stephanopoulos & Reklaitis, 2011).

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 (Pistikopoulos et al., 2021). An overview of the main modeling techniques is shown in the next sections based on the classification proposed by Martín and Grossmann (2012).

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 Couper, Penney, Fair, and Walas (2005), Hall (2012), Sadhukhan, Ng, and Hernandez (2014).

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 (Szirtes, 2007).

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 (Loeppert, Schwab, & Goldberg, 1995) and phase (Brignole & Pereda, 2013) equilibrium models, kinetic models (Buzzi-Ferraris & Manenti, 2009), population balances (Ramkrishna, 2000), and computer fluid dynamics (CFD) (Anderson & Wendt, 1995) 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 (Queipo et al., 2005).

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 (Wilson & Sahinidis, 2017), 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 (Quirante, Javaloyes, & Caballero, 2015), 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 (Himmelblau, 2000).

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 (Belton & Stewart, 2002).

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 (Giove, Brancia, Satterstrom, & Linkov, 2009).

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

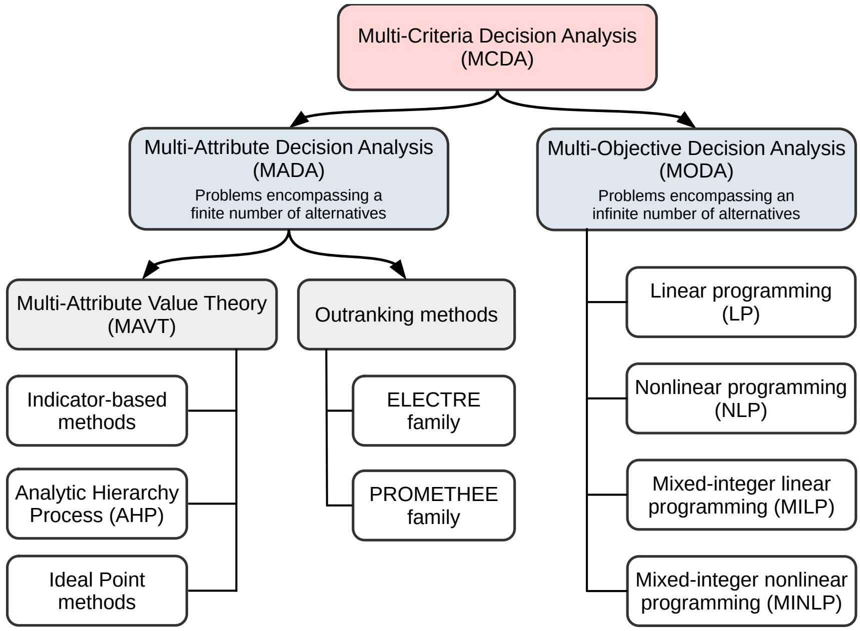

Figure 1.3: Classification of MCDA methods.

an utility or value function. A number of utility functions have been proposed in the literature, including standardization, min-max, and target utility functions (OECD and European Commission, 2008). 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 (Gasser et al., 2020). 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 (Marichal & Roubens, 2000). 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 and Lahdelma (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 (Saaty, 2000).

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 (Hwang & Yoon, 1995).

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 (Giove et al., 2009). Some of the most popular outranking methods are ELECTRE I (Bernard Roy, 1968), II (Bertier Roy & Bertier, 1973), and III (Bernard Roy et al., 1978), and PROMETHEE (Vincke & Brans, 1985).

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 (Giove et al., 2009). 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 (Giove et al., 2009).

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 (Grossmann, 2021).

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

The two most widely used methods to solve LP problems are the Simplex algorithm (Murty, 1983) and interior-point methods (Potra & Wright, 2000). 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 (Grossmann, 2021). These methods are implemented in solvers such as CPLEX (IBM, 2009), Gurobi (Gurobi Optimization, LLC, 2021), or XPRESS (FICO, 2021).

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 (Floudas, 1995).

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

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 (Gill, Murray, & Saunders, 2005). SNOPT is a solver based on this method (Gill et al., 2005).

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 (Murtagh & Saunders, 1983) or CONOPT (Drud, 1985) 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 Wächter and Biegler, 2006 and KNITRO (Waltz & Nocedal, 2004) 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 (Grossmann, 2021).

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

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 (Floudas, 1995).

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 (Grossmann, 2021). Gurobi (Gurobi Optimization, LLC, 2021) and CPLEX (IBM, 2009) 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 (Grossmann, 2021).

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

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 (Floudas, 1995).

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 (Floudas, 1995).

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 (Gharehbaghi & Scott-Young, 2018). 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 through the techno-economic assessment of the technologies under evaluation embedded in a mixed-integer nonlinear programming model.

CHAPTER 3 - GEOSPATIAL 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 ?? - 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.

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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 (Ruttenberg, 2001). 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 (A.S. Sampat, Ruiz-Mercado, & Zavala, 2018). 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, DelSontro, & Downing, 2019).

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, Drangert, & White, 2009). 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, 2011), 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 (United States Department of Agriculture (USDA), 2009), 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 (United States Department of Agriculture (USDA), National Agricultural Statistics Service, 2020). Thus, this shows potential phosphate U.S. releases of $562.6 \cdot 10^6$ kg/yr. A.S. Sampat, Martín, Martín, and Zavala (2017) 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 (Muhmood, Lu, Dong, & Wu, 2019), 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 (Martín-Hernández, Sampat, Zavala, & Martín, 2018). Struvite is a phosphate-based mineral, which can be applied as a slow release fertilizer (Richards & Johnston, 2001), 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, De Angelis, Pavan, Prisciandaro, & Cecchi, 2001), mineral fertilizer industry (Matynia et al., 2013), or agricultural industry (Shashvatt, Benoit, Aris, & Blaney, 2018). Thermodynamic models representing the formation of struvite and other precipitates have been also developed for various wastes including liquid swine manure (Celen, Buchanan, Burns, Robinson, & Raman, 2007), human urine (Harada et al., 2006; Ronteltap, Maurer, & Gujer, 2007), and municipal wastewater (Rahaman, Mavinic, Meikleham, & Ellis, 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 et al., 2014; Mangin & Klein, 2004). 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 & Shih, 2016), 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, Fattah, & Huchzermeier, 2016). 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 (U.S. Geological Survey, 2013).

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, 2011; Alexander et al., 2008; Smith & Alexander, 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 (International Plant Nutrition Institute (IPNI), 2012). Phosphorus content for several commercial phosphate fertilizers and different manure types can be found in Ohio State University Extension (2017) and Ohio State University Extension (2005) 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.

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

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 (Pickard, Daniel, Mehaffey, Jackson, & Neale, 2015). 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) (United States Department of Agriculture (USDA), 2019). 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 (United States Department of Agriculture (USDA), 2009). 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 (2016).

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 Bakshi, Ziv, and Lepech (2015) has been considered, Eq. 3.2. 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 et al., 2016). 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, 2012).

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

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

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 physicochemical characteristics of the livestock organic material (Tao et al., 2016), see Table 3.2. Please note that pH refers the adjusted pH for optimal struvite precipitation (Tao et al., 2016; Zeng & Li, 2006).

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

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 et al., 2016; Metcalf & Eddy, 2014). Finally, activities for each compound are calculated using Eq. 3.8

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

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

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

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

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 & Pinching, 1949)
Water	$H_2O \leftrightarrow OH^- + H^+$	14	(Skoog, West, Holler, & Crouch
Phosphoric acid	$H_3PO_4 \leftrightarrow H_2PO_4^- + H^+$	2.1	(Ohlinger, Young, & Schroeder
	$H_2PO_4^- \leftrightarrow HPO_4^{2-} + H^+$	7.2	(Ohlinger, Young, & Schroeder
	$HPO_4^{2-} \leftrightarrow PO_4^{3-} + H^+$	12.35	(Ohlinger, Young, & Schroeder
Carbonic acid	$H_2CO_3 \leftrightarrow HCO_3^- + H^+$	6.35	(Skoog, West, Holler, & Crouch
	$HCO_3^- \leftrightarrow CO_3^{2-} + H^+$	10.33	(Skoog, West, Holler, & Crouch

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 et al., 2016; Harada et al., 2006; Gadekar & Pullammanappallil, 2010). A general solubility equilibrium, where n_a and m_b are the stoichiometric

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, Young, & Schroeder, 1998)
K-struvite	$MgKPO_4 \cdot 6H_2O \leftrightarrow Mg^{2+} + K^+ + PO_4^{3-}$	10.6	(Taylor, Frazier, & Gurneynium, 1963)
Hydroxyapatite	$Ca_5(PO_4)_3OH \leftrightarrow 5Ca^{2+} + 3PO_4^{3-} + OH^-$	44.33	(Brezonik & Arnold, 2011)
Calcium carbonate	$CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-}$	8.48	(Morse, Arvidson, & Lüttge, 2007)
Tricalcium phosphate	$Ca_3(PO_4)_2 \leftrightarrow 3Ca^{2+} + 2PO_4^{3-}$	25.50	(Fowler & Kuroda, 1986)
Dicalcium phosphate	$CaHPO_4 \leftrightarrow Ca^{2+} + HPO_4^{2-}$	6.57	(Gregory, Moreno, & Brown, 1970)
Calcium hydroxide	$Ca(OH)_2 \leftrightarrow Ca^{2+} + 2OH^-$	5.19	(Skoog, West, Holler, & Crouch, 2014)
Magnesium hydroxide	$Mg(OH)_2 \leftrightarrow Mg^{2+} + 2OH^-$	11.15	(Skoog, West, Holler, & Crouch, 2014)

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 (Tao et al., 2016). 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.

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

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

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

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

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 (Dunning, Huchette, & Lubin, 2017; Bezanson, Edelman, Karpinski, & Shah, 2017). The statistical study of cattle waste composition data, the Monte Carlo framework, result analysis, and data visualization were made in Python language (van Rossum, 1995; van der Walt, Colbert, & Varoquaux, 2011; Hunter, 2007, 2010).

3.2.3.8 *Model validation and limitations*

The developed model was validated using the data provided by Zeng and Li (2006). 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, Young, and Schroeder (1998), 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 et al., 2016; Zeng & Li, 2006).

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 et al. (2016) 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.

$$x_{\mathrm{struvite}\left(\mathrm{PO}_4^{3-}\right)} = \frac{0.798}{1 + \left(x_{\mathrm{Ca}^{2+}:\mathrm{PO}_4^{3-}} \cdot 0.576\right)^{2.113}} \tag{3.19}$$

$$x_{\mathrm{hydroxyapatite}\left(\mathrm{Ca}^{2+}\right)} = -4.321 \cdot 10^{-2} \cdot x^2_{\mathrm{Ca}^{2+}:\mathrm{PO}_4^{3-}} + 0.313 \cdot x_{\mathrm{Ca}^{2+}:\mathrm{PO}_4^{3-}} - 3.619 \cdot 10^{-2} \tag{3.20}$$

$$x_{\mathrm{CaCO_3}\left(\mathrm{Ca}^{2+}\right)} = \frac{1.020}{1 + \left(x_{\mathrm{Ca}^{2+}:\mathrm{PO}_4^{3-}} \cdot 0.410\right)^{1.029}} \tag{3.21}$$

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 $|CaCO_3$).

$$x_{\text{struvite}\left(PO_4^{3-}\right)} = \frac{0.695}{1 + \left(x_{\text{Alk}} \cdot 4.229 \cdot 10^{-4}\right)^{-2.638}} \tag{3.22}$$

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

$$x_{CaCO_3\left(Ca^{2+}\right)} = \frac{0.847}{1 + \left(x_{\text{Alk}} \cdot 4.646 \cdot 10^{-4}\right)^{-1.870}} \tag{3.24}$$

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 (United States Department of Agriculture (USDA), 2019), 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 (Martín-Hernández et al., 2018). 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 (International Plant Nutrition Institute (IPNI), 2012) 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

(United States Department of Agriculture (USDA), 2019). 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) (United States Department of Agriculture, 2000). 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 et al. (2017), A.M. Sampat et al. (2019), and Hu, Sampat, Ruiz-Mercado, and Zavala (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 $\left(\frac{\mu S}{cm}\right)$
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
$x_{struvite(PO_4^{3-})}$	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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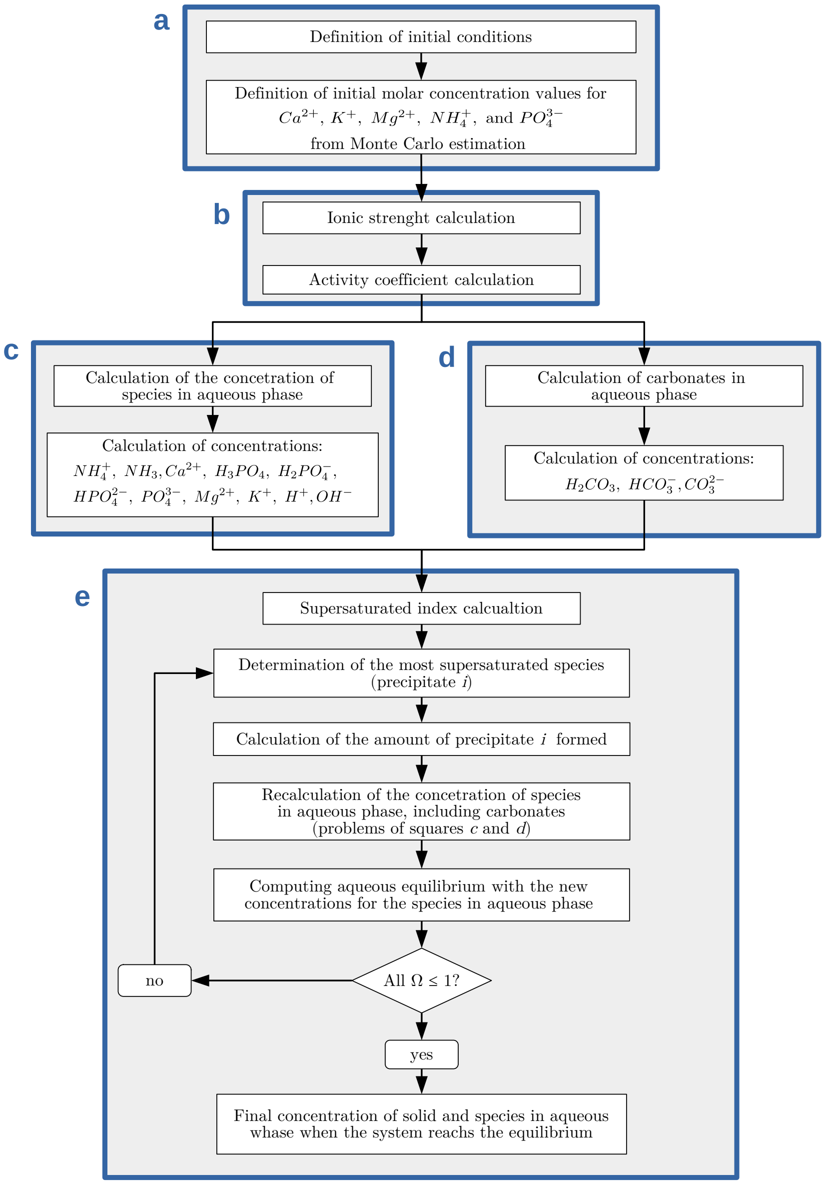


Figure 3.1: Flowchart of the proposed algorithm to solve the thermodynamic model for the formation of precipitates in cattle organic waste.

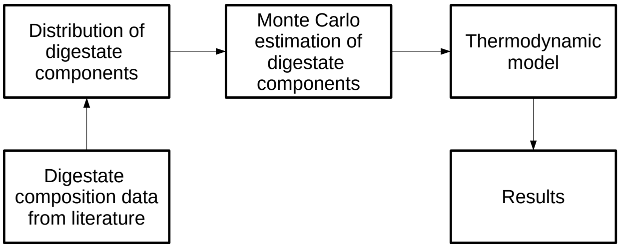


Figure 3.2: A solution procedure to evaluate the influence of the cattle waste composition variability in the formation of struvite.

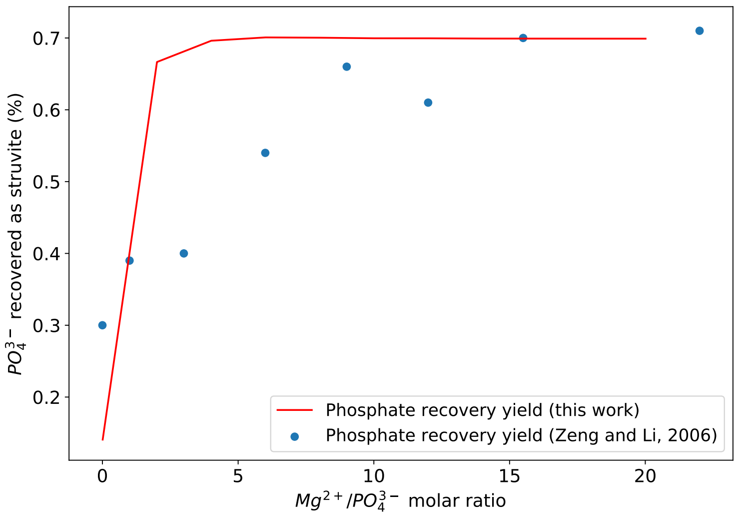


Figure 3.3: Comparison between experimental results reported by Zeng and Li (2006) and the results provided by the model developed in this work.

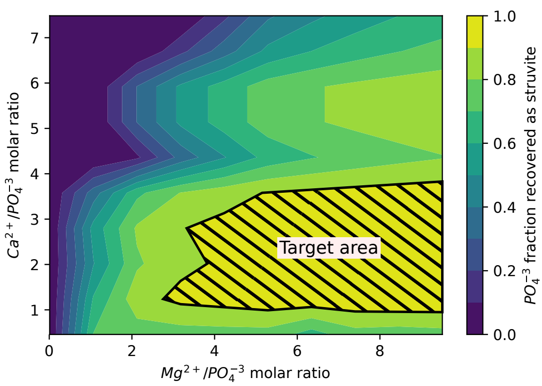


Figure 3.4: Influence of magnesium and calcium in struvite precipitation.

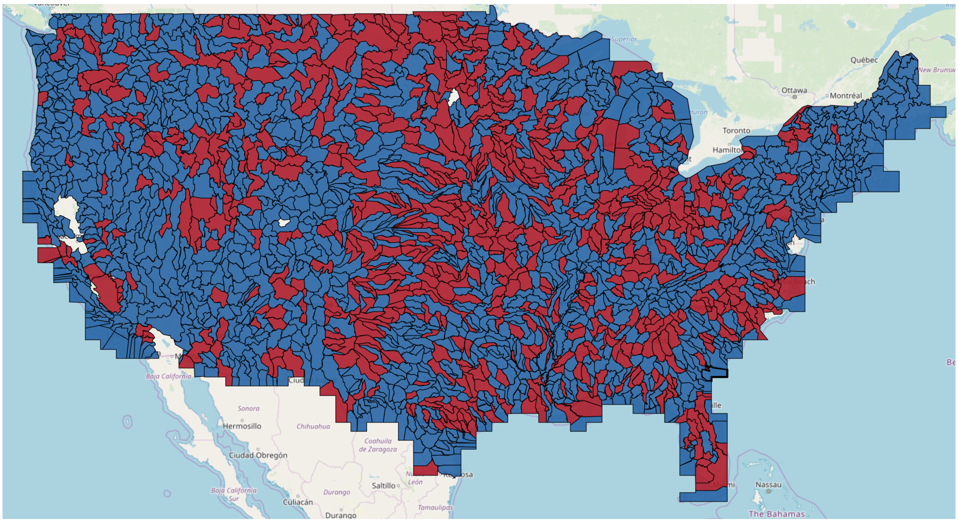
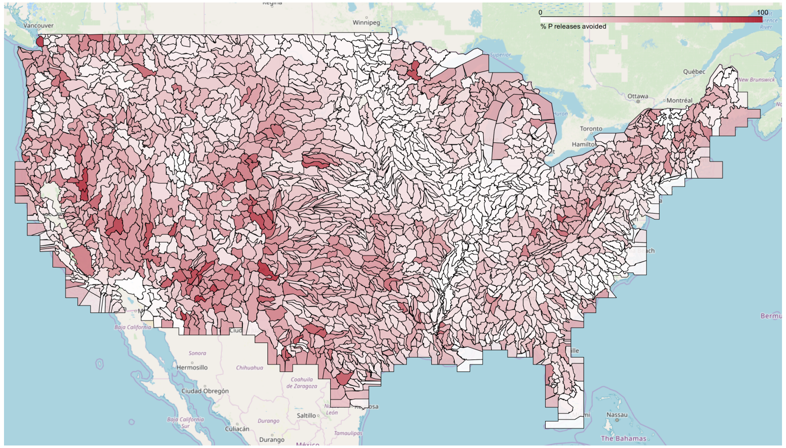
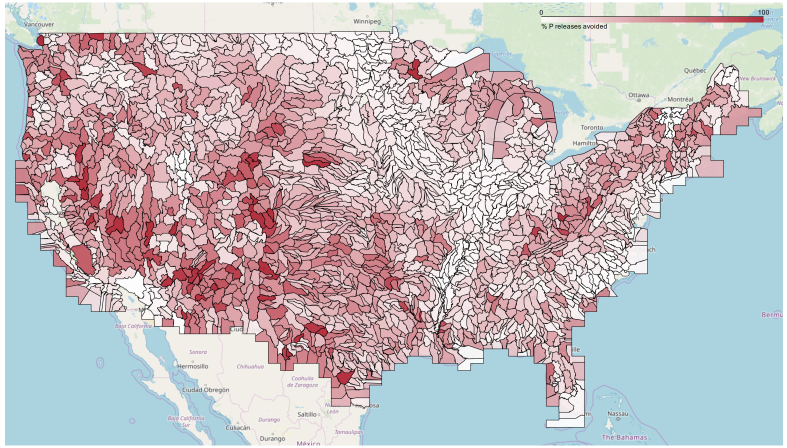


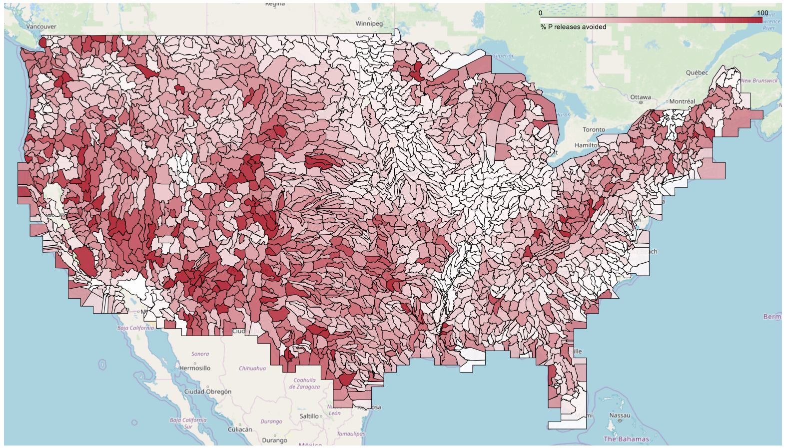
Figure 3.5: Techno-ecological synergy (TES) metric values for HUC8 watersheds. Red indicates watersheds with unbalanced agricultural phosphorus releases, and blue indicates watersheds with balanced agricultural phosphorus releases. White indicates watersheds with not available data.



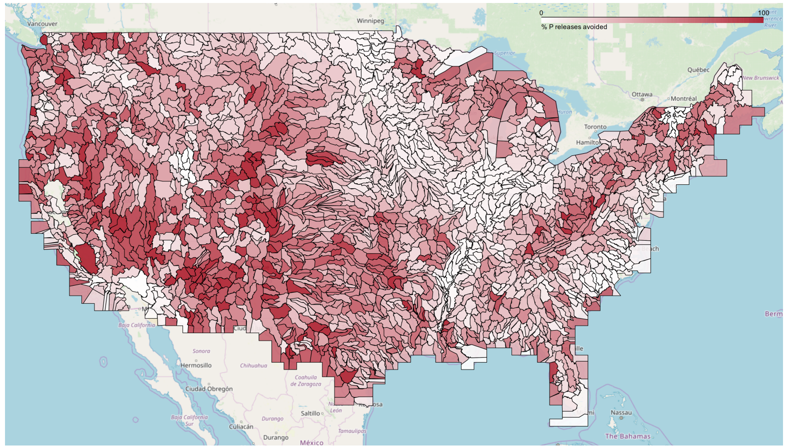
(a) Scenario 1



(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

Part II

NITROGEN MANAGEMENT AND RECOVERY

Part III

INTEGRATION OF ANAEROBIC DIGESTION AND NUTRIENT MANAGEMENT SYSTEMS

Part IV

APPENDIX