MODELING AND OPTIMIZATION OF SYSTEMS FOR NUTRIENT RECOVERY FROM LIVESTOCK WASTE

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

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.

— Séneca, De la brevedad de la vida.

ACKNOWLEDGMENTS

Complete

ABSTRACT

To be completed.

RESUMEN

Completar.

PUBLICATIONS

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

[1] E. Martín-Hernández, L.S. Guerras, and M. Martín. «Optimal technology selection for the biogas upgrading to biomethane.» In: *Journal of Cleaner Production* (2020), p. 122032.

[2] E. Martín-Hernández, Y. Hu, V.M. Zavala, M. Martín, and G.J. Ruiz-Mercado. «Analysis of incentive policies for phosphorus recovery at livestock facilities in the Great Lakes area.» In: *Resources, Conservation & Recycling* (Under Review).

[3] E. Martín-Hernández, M. Martín, and G.J. Ruiz-Mercado. «A geospatial environmental and techno-economic framework for sustainable phosphorus management at livestock facilities.» In: *Resources, Conservation & Recycling* (Under Review).

[4] E. Martín-Hernández, G.J. Ruiz-Mercado, and M. Martín. «Model-driven spatial evaluation of nutrient recovery from livestock leachate for struvite production.» In: *Journal of Environmental Management* 271 (2020), p. 110967.

[5] E. Martín-Hernández, A.M. Sampat, M. Martin, V.M. Zavala, and G.J. Ruiz-Mercado. «A Logistics Analysis for Advancing Carbon and Nutrient Recovery from Organic Waste.» In: *Advances in Carbon Management Technologies*. CRC Press, 2021, pp. 186–207.

[6] E. Martín-Hernández, A.M. Sampat, V.M. Zavala, and M. Martín. «Optimal integrated facility for waste processing.» In: *Chemical Engineering Research and Design* 131 (2018), pp. 160–182.

[7] M. Mohammadi, E. Martín Hernández, M. Martín, and I. Harjunkoski. «Modeling and Analysis of Organic Waste Management Systems in Centralized and Decentralized Supply Chains Using Generalized Disjunctive Programming.» In: *Industrial & Engineering Chemistry Research* 60.4 (2021), pp. 1719–1745.

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ACRONYMS

1 INTRODUCTION

1.1 RATIONALE: OVERVIEW OF THE NUTRIENT PULLUTION CHALLENGE

Human population is experiencing a continuous growth since end of the Black Death in the XIV century [2], 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 [19]. Population growth demands increasing amounts of food, which in turn requires an efficient food production system to support this growth. 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 [16], the development of the Haber-Bosch process for the production of synthetic nitrogen-based fertilizers in 1913 [17], and the mechanization of agriculture and the development of the modern intensive farming in the XX century [7, 14].

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 these activities [3]. 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 waters, which can lead algal bloom episodes. Algal 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, altering the normal functioning of the aquatic ecosystem. Some algal blooms can releases toxins, and they cause hypoxia as a consequence of the aerobic degradation of algal biomass by bacteria.

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.

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, and no substitute material is currently known [8]. 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 techniques and ensure the global food security.

Attending to the nutrient releases from livestock intensive 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 [12]. 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 [21]. Commonly, manure management is 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 [18]. The obtained 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 [18]. However, both materials, the liquid effluent obtained from the lagoons, and compost, are too bulky to be economically transported to nutrient deficient locations [4]. 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 croplands, which might lead the harmful environmental impacts previously described.

2 CAFO is a regulatory term defined by the US Environmental Protection Agency for large facilities where animals are kept and raised in confined situations [22]. This term will be used throughout the dissertation to denote the intensive livestock farming facilities studied.

Therefore, the implementation of processes for the recovery of phosphorus and nitrogen at CAFOs is a promising alternative for abating nutrient releases and reducing the environmental footprint of livestock industry, 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 ob phases separation; and processes focused on nitrogen recovery, such as stripping, membrane separation, waste drying coupled with ammonia scrubbing, and phases 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 final 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 od each region, the current or potential installation of anaerobic digestion systems, etc. Additionally, in the decision-making process these factors have to be prioritized to select the most suitable process for each particular facility, i.e., in regions with a low risk of eutrophication, more economical processes for nutrient recovery could be installed in even though their recovery efficiency may be lower than other alternatives. 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 regarding eutrophication risk at the subbasin level and data from the techno-economic analysis of the processes studied.

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 in the limitation of fertilizer application in croplands. The application of fertilizer and manure for nitrogen supplementation en the European Union (EU) is currently regulated by the Nitrates Directive (91/676/EEC) [11]. Regarding the limitations for phosphorus application, these are defined at national level. Several European countries have implemented application standards based on the different crops and materials used as fertilizers. Generally, phosphorus application limits are more restrictive in northwestern Europe [1]. 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 [15]. New efforts for the adoption of bio-fertilizers obtained from organic waste are being currently performed in the development of the "Integrated Nutrient Management Plan" (INMAP), which is part of the 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 [6, 10]. 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 framewrok for their use and trade.

In the United States, CAFOs are regulated under the Clean Water Act as point source waste discharge. This regulation sets the need of permits for discharging pollutants to water, called National Pollutant Discharge Elimination System (NPDES) permits, including the release of nitrogen of phosphorus. This permit must include the necessary provisions for avoiding the harmful effects of the discharges on water and human health [20]. The development and implementation of a Nutrient Management Plan (NMP) is a required element to get a NPDES permit. This document must identify the management practices to be implemented at the 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 are defined under federal regulation [9]. 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 [13]. However, 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. Moreover, US EPA acknowledges that highly refined and primarily inorganic products (such as struvite) could be outside of the scope of these restrictions [5]. However, 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, 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 either in the EU and the US. However, both regions have developed programs to study and promote the implementation of other technologies for the treatment of livestock waste, specially the deployment of anaerobic digestion systems. 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 with anaerobic digestion for the production of electricity. 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.

This thesis 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.

1.2 SCOPE AND OBJECTIVES OF THE THESIS

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.

OBJECTIVE I: To perform a review of the state-of-the-art of the processes for phosphorus and nitrogen recovery from livestock waste, identifying those processes whose implementation at CAFOs is feasible from a techno-economic perspective.

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.

1.3 THESIS OUTLINE

This dissertation is structured in three parts. Part I is devoted to the study of phosphorus management and recovery, Part II address a techno-economic assessment of the technologies for nitrogen recovery, and Part III conduct a research for determining the best combination of units for biomethane production in order to integrate biogas production and nutrient recovery processes.

1.3.1 *Part I - Phosphorus management and recovery*

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

CHAPTER **??** - ASSESSMENT OF PHOSPHORUS RECOVERY THROUGH STRUVITE PRECIPITATION. This chapter study 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 and robust thermodynamic model. In addition, the variability in the organic waste composition is captured through a probability framework based on 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.

1.3.2 *Part II - Nitrogen management and recovery*

CHAPTER ?? - MULTI-SCALE TECHNO-ECONOMIC ASSESSMENT OF NITROGEN RECOVERY SYSTEMS FOR SWINE OPERATIONS. This chapter performs a review of 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.

1.3.3 *Part III - Nitrogen management and recovery*

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

BIBLIOGRAPHY

[1] Fien Amery and Oscar Frédéric Schoumans. *Agricultural phosphorus legislation in Europe*. Institute for Agricultural, Fisheries Research (ILVO), and Alterra Wageningen UR, 2014.

[2] Jean Noël Biraben. «An essay concerning mankind's demographic evolution.» In: *Journal of Human Evolution* 9.8 (1980), pp. 655–663.

[3] A. F. Bouwman, A. H. W. Beusen, and G. Billen. «Human alteration of the global nitrogen and phosphorus soil balances for the period 1970–2050.» In: *Global Biogeochemical Cycles* 23.4 (2009). DOI: https://doi.org/10.1029/2009GB003576.

[4] Robert T Burns and Lara B Moody. «Phosphorus recovery from animal manures using optimized struvite precipitation.» In: *Proceedings of Coagulants and Flocculants: Global market and technical opportunities for water treatment chemicals* (2002), pp. 1–4.

[5] CNP. *Review of Applicability of EPA's Part 503 Biosolids Rule on Phosphorus Minerals recovered at Water Resource Recovery Facilities*. Tech. rep. CNP, 2021.

[6] European Comission. *A new Circular Economy Action for a cleaner and more competitive Europe*. Tech. rep. European Comission, 2020.

[7] George Constable and Bob Somerville. *A century of innovation: Twenty engineering achievements that transformed our lives. Chapter 7, Agricultural mechanization*. Joseph Henry Press, 2003.

[8] Dana Cordell, Jan-Olof Drangert, and Stuart White. «The story of phosphorus: global food security and food for thought.» In: *Global environmental change* 19.2 (2009), pp. 292–305.

[9] US EPA. *Elements of an NPDES Permit for a CAFO. NPDES Permit Writers' Manual for CAFOs*. Tech. rep. U.S. Environmental Protection Agency, 2020.

[10] ESSP. *ESPP input for the EU's "Integrated Nutrient Management Action Plan" (INMAP)*. Tech. rep. European Sustainable Phosphorus Platform, 2021.

[11] B. Grizzetti et al. «How EU policies could reduce nutrient pollution in European inland and coastal waters.» In: *Global Environmental Change* 69 (2021), p. 102281.

[12] Robert L. Kellogg, Charles H. Lander, David C. Moffitt, and Noel Gollehon. *Manure Nutrients Relative to the Capacity of Cropland and Pastureland to Assimilate Nutrients: Spatial and Temporal Trends for the United States*. Tech. rep. U.S. Department of Agriculture, 2000.

[13] NACWA. *Issue Outline on Resource Recovery from Wastewater and Coverage of 40 C.F.R. Part 503*. Tech. rep. National Association of Clean Water Agencies, 2014.

[14] Danielle Nierenberg and Lisa Mastny. *Happier meals: Rethinking the global meat industry*. Vol. 171. Worldwatch Institute, 2005.

[15] Isabelle Piot-Lepetit. *Agricultural externalities and environmental regulation: The case od manure management and spreading land allocation*. Bentham Science Publishers, 2011.

[16] Sayma Samreen and Sharba Kausar. «Phosphorus Fertilizer: The Original and Commercial Sources.» In: Phosphorus - Recovery and Recycling. IntechOpen, 2019. ISBN: 978-1-83881-021-4. DOI: 10.5772/intechopen.82240.

[17] Vaclav Smil. «Detonator of the population explosion.» In: *Nature* 400.6743 (1999), pp. 415–415.

[18] Elizabeth Tilley, Lukas Ulrich, Christoph Lüthi, Philippe Reymond, and Christian Zurbrügg. *Compendium of sanitation systems and technologies*. Eawag, 2014.

[19] United Nations, Department of Economic and Social Affairs. *World Population Prospects 2019*. https://population.un.org/wpp/Graphs/Probabilistic/POP/TOT/900. [Online; accessed 22-August-2021]. 2019.

[20] US EPA. *NPDES Permit Basics*. https://www.epa.gov/npdes/npdes-permit-basics. [Online; accessed 24-August-2021]. 2020.

[21] USDA. *Agricultural Wate Management Field Handbook*. Tech. rep. U.S. Department of Agriculture, 2009.

[22] USDA. *Animal Feeding Operations (AFO) and Concentrated Animal Feeding Operations (CAFO)*. https://www.nrcs.usda.gov/wps/portal/nrcs/main/national/plantsanimals/livestock/afo/. [Online; accessed 10-August-2021]. 2011.

Part I

PHOSPHORUS MANAGEMENT AND RECOVERY

Complete introduction of Part I

Part II

NITROGEN MANAGEMENT AND RECOVERY

Part III

INTEGRATION OF ANAEROBIC DIGESTION AND NUTRIENT MANAGEMENT SYSTEMS

Part IV

APPENDIX