Contents lists available at ScienceDirect





journal homepage: www.elsevier.com/locate/scp



Phosphorous flow analysis and resource circularity at the province level in north Italy



César Mejia Duque Torres^a, Luca Ciacci^{b,c,*}, Fabrizio Passarini^{b,c,**}

^a Department of Economics, Alma Mater Studiorum, University of Bologna, Via Angherà 22, 47921, Rimini, Italy

^b Department of Industrial Chemistry "Toso Montanari", Alma Mater Studiorum, University of Bologna, Viale Risorgimento 4, 40136, Bologna, Italy

^c Interdepartmental Centre for Industrial Research "Renewable Resources, Environment, Sea and Energy, Alma Mater Studiorum – University of

Bologna, Via D. Campana 71, 47923, Rimini, Italy

ARTICLE INFO

Keywords: Substance flow analysis Wastewater treatment Phosphorous recovery Circular economy Digestate sludge

ABSTRACT

Phosphorus is an essential element for living organisms, but its unequal distribution combined with the current anthropogenic activity make it a critical resource. To decrease the risks of future shortages, new techniques to manage phosphorous are needed to be mainstreamed under a Circular Economy approach to boost a sustainable transition. A full characterization of flows and stocks is necessary to measure the contribution of secondary materials to meet the overall demand in a system and support decision-making process towards potential improvements. This understanding is determinant for a successful implementation of phosphorous recovery at the regional level, where site-specific conditions dictate local constraints.

In this study, material flow analysis has been applied to characterize the 2020 phosphorous cycle in the Province of Rimini (Italy) and the State of San Marino, which are served by a wastewater treatment plant with a 560,000 person-equivalent capacity. Our model shows that, about 236 ± 23 t P entered the system, while 155 ± 14 t P left it, resulting in a net accumulation of 81 ± 21 t P, mainly located in soil for crop production, water bodies, and sedimentation due to dissipative flows. The greatest potential for phosphorous recovery is embedded into the digested sludge from the wastewater treatment plant, which would ideally meet 96% of the annual local demand of mineral fertilizers. However, this flow is currently disposed of by landfilling. Further technical, economic, environmental, and regulatory valuations are ultimately needed to build a positive business case to recover phosphorous in the region.

1. Introduction

1.1. Overview

Phosphorus (P) is an essential and irreplaceable element for living organisms, playing an essential function in the human metabolism as well as in the global agriculture and food production systems. Although P is the tenth most abundant element in the earth's crust (Rattan and Stewart, 2017), the supply risk level and the economic importance of P and phosphate rocks rank as nearly critical for

https://doi.org/10.1016/j.scp.2023.101133

Received 25 February 2023; Received in revised form 6 May 2023; Accepted 20 May 2023

Available online 27 May 2023

^{*} Corresponding author. Department of Industrial Chemistry "Toso Montanari", Alma Mater Studiorum, University of Bologna, Viale Risorgimento 4, 40136, Bologna, Italy.

^{**} Corresponding author. Department of Industrial Chemistry "Toso Montanari", Alma Mater Studiorum, University of Bologna, Viale Risorgimento 4, 40136, Bologna, Italy.

E-mail addresses: luca.ciacci5@unibo.it (L. Ciacci), fabrizio.passarini@unibo.it (F. Passarini).

^{2352-5541/© 2023} The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

the U.S. (McCullough and Nassaer, 2017) and critical for the European Union (EU) (European Commission, 2020) mainly because the growing global and European demand for this element is coupled with virtually non-existent reserves within the Member States, with the exception of Finland (Zhu et al., 2023). The location and concentration of its natural deposits occur in a small number of countries including Morocco, Jordan, South Africa, the United States, and China. All together, they represent up to 90% the world-known reserves of P (Rattan and Stewart, 2017). This unevenness in the availability of P reserves forces countries to depend on P imports to sustain their agricultural needs. Moreover, the irreplaceability of this nutrient causes fluctuations in the prices of food whenever the price of P fertilizers change (Wang et al., 2022). On top of that, the extraction of P in mines and the long time in which the circulation of P occurs in the natural environment poses the thread of experiencing scarcity in relation to the economically extractable P around the world (Childers et al., 2011).

Its extensive use in agriculture (about 95% of P used as fertilizer in this sector globally (Sena et al., 2021)), makes this element undergo intentionally dissipative uses (Ciacci et al., 2015), causing P flows to migrate from the anthroposphere to the biosphere according to a linear model of production and consumption still depictable as "take-make-dispose". Although this dispersion into the environment does not make future P recovery impossible, the achievement of a restorative model for this element (Reike et al., 2018; Ellen McArthur Foundation, 2013) is certainly challenging. Despite this, adopting a circular economy model for P would improve the net use efficiency of this resource, reduce the risk of shortages and geopolitical frictions, minimize price volatility, and improve the resilience of food systems (Egle et al., 2015).

This potential recyclability is under consideration to improve the overall effectiveness in the P cycle. The literature on P recovery indicates that wastewater treatment plants (WWTPs) represent an interesting spot to locate technologies able to recover high-quality P products (van Dijk et al., 2016; Egle et al., 2015; Childers et al., 2011; Cordell et al., 2009). Many processes to remove P at wastewater treatment plants have been developed, the most promising of which are covered in the EU list of the Best Available Techniques (BATs), (Brinkmann et al., 2016). Common methods exploited by BATs include crystallization, nanofiltration/reverse osmosis, evaporation, aerobic treatment, enhanced biological P removal, and chemical precipitation. However, their adoption is mainly driven to meet the water quality standards by reducing the P concentration in the effluents of the WWTPs rather than on further recovering and using P (Karunanithi et al., 2016). Nonetheless, the output of these technologies might concentrate P in sewage sludge for subsequent valorization (Egle et al., 2015).

The necessity for developing and adopting feasible technologies and practices to recycle this element has moved policy makers to introduce transnational and national regulations. For instance, the European Commission is expected to include P recovery form wastewater as one of the economic activities that will qualify as contributing substantially to the transition to a Circular Economy under the Taxonomy Regulation (European Commision, 2023). Some EU countries have followed, or even anticipated, the establishment of a legal framework to remove and recover P (Zhu et al., 2023). Such is the case of Italy, whose Implementation Action Plan 2020–2025 for the Italian Bioeconomy Strategy includes wastewater and sludge valorization into compost, biochar, biomethane, chemical substances and materials for the benefit of local areas as one the five flagship projects to be developed in the short term (Presidenza dei Consiglio dei Ministri, 2021).

Similarly to other countries in south Europe, Italy has relatively smaller stocks of P in the agricultural topsoil than Member States in north Europe (on average, 60 kg P ha⁻¹ versus >100 kg P ha⁻¹, respectively) and ranks among the highest EU country users of P fertilizers, applying more than 9 kg P ha⁻¹ yr⁻¹. However, this input is then contrasted by an estimated P loss of the same magnitude due to severe erosion, which implies a four-times higher environmental risk (e.g., eutrophication) to river basins than the European average. (Panagos et al., 2022).

Considering the importance of the agricultural sector in the northern regions of Italy, in which up to 65% of the national fertilizer consumption occurs (Centro di ricerca Politiche e Bioeconomia, 2021), past eutrophication events, and the legal framework supporting circular economy initiatives, we believe that there might be an enormous socio-economic potential for Italian provinces to benefit from local P recovery.

1.2. Research issue and aim of this study

Systematic identification and quantification of P flows that are potentially available in a system for recovery and reuse is crucial to evaluate beneficial effects of implementing solutions for material circularity and improve resource management (Wang et al., 2022; Papangelou et al., 2020; Egle et al., 2014). More specifically, the setting of strategies for the recovery of essential and critical resources such as P from currently unexploited waste streams would have the dual effect of enhancing sustainability and resilience in material supply chains as well as pursuing the goals of waste prevention and minimization, maximize the use of non-renewable resources into anthropogenic cycles, and reduce their potential impact on the environment as mainstreamed by Green Chemistry principles.

To this aim, material flow analysis (MFA) can enable proper characterization of the flows and stocks of materials within a certain system at a specific space and time (Brunner and Rechberger, 2005). It is commonly applied to understand how materials or energy are metabolized in natural-anthropogenic systems at different scales that can range from processes, isolated populations, regions, countries, groups of countries to the entire world, providing quantifiable information to support decision-making processes in the fields of resource management, waste management, and environmental management. Based on the principle of mass conservation, MFA detects how and where a given resource is transported, stored, or metabolized through different processes and sinks.

Of relevance here, MFA has been previously used for (i) conceptualizing and mapping the anthropogenic metabolism of P (Baroi et al., 2020), (ii) indicating and comparing how regions use, reuse and lose P (Wang et al., 2022); van Dijk et al. (2016); (iii) showing the heterogeneity of the P metabolism between countries, regions and within countries (van Dijk et al., 2016); (iv) identifying and quantifying flows of P that are potentially available for their recovery, assessing the level of circularity of P within a determined system, and evaluating recovery and recycling solutions towards a better circular resource management (Houssini et al., 2023; El Wali

et al., 2021; Papangelou et al., 2020; Treadwell et al., 2018; Koppelaar and Weikard, 2013; Brunner, 2010); (v) developing a framework for categorizing P into reserve and resource identification and evaluation (Lederer et al., 2014); (vi) overcoming deficiencies in the reliability and availability of data (Baroi et al., 2020; Zoboli et al., 2015); (vii) examining specific problems and opportunities that might differ across different geographies and jurisdictions (Egle et al., 2014).

Although the anthropogenic metabolism of P is applicable with relative minor adjustments to different geographical scale thanks to a well-established supply chain and use of this resource in modern society, site-specific mass balances are needed to account for the intrinsic variations in material accumulation and depletion dynamics from stocks at the regional or province scale. Ultimately, this thorough system understanding of P flows and stocks is vital to a successful development of recovery techniques and prioritizing sources for accessing a sustainable supply of P.

To this aim, we have explored the potential for P circularity at the province level, in the system comprising seven municipalities in the Province of Rimini plus the independent State of San Marino located in north Italy. Altogether, they configure the urbanagricultural system that is served by the WWTP of Santa Giustina, located in the Province of Rimini, with a capacity of 560,000 person-equivalent (p.e.). In particular, In the present work, an MFA model has been developed and applied to (i) characterize the P anthropogenic cycle, (ii) define the current levels of material circularity, (iii) identify spots where action should be taken to reduce P leakages and benefit from the initiatives aiming to improve P management in the system under scrutiny.

2. Materials and methods

2.1. System definition

Rimini is a province situated in the Emilia-Romagna region of Italy and the north region of the Adriatic Sea. It has an area of 865 km² and a population of about 340,000 inhabitants. Its tourist's affluence plays a particular role in the province due to its relatively large size. In 2018, about 2,252,000 tourists arrived in the municipalities of Rimini. They had an average stay of 4.3 days, which equals an additional yearly population of about 26,500 inhabitants (Servizio Statistica e Sistemi Informativi Geografici, 2019).

According to the regional Chamber of Commerce, the total agricultural land in this Province covered about 34,400 ha (ha, 1 ha = $10,000 \text{ m}^2$) and the total production amounted to 304,570 tonnes (t, 1 t = 1000 kg). In 2019, 19,440 t of fertilizers were distributed in the province, of which 7830 t correspond to mineral compounds, organic and organic-mineral fertilizers, 9370 t are soil amendments, 2160 t are crop substrates, and 80 t of "specific action products" such as pesticides, fungicides, insecticides, and similar (Camera di commercio della Romagna-Forli-Cesena e Rimini, 2020. Agricoltura 2019. Le statistiche dell'agricoltura in provincia di Rimini. Camera di commercio della Romagna-Forli-Cesena e Rimini, 1-32.).

In 2015, the new WWTP of Santa Giustina was inaugurated to serve the communes of Rimini, Coriano, Santarcangelo, Verucchio, Poggio Torianna, Bellaria Igea-Marina, San Leo, and the State of San Marino. The total plant capacity results from the addition of a new line of treatment with a capacity of 340,000 p.e. to the traditional line with a capacity of 220,000 p.e. The new line was built to guarantee that by 2024 there will not be bathing prohibitions along the Rimini coast because of low-quality water levels. It aims to eliminate incoming and untreated black water from the 11 discharges of water to the sea from the region. Besides increasing the capacity in the plant of Santa Giustina, the project included a set of tanks to cope with the variability of water inflow during rainy events in summer, where the system experiences its peak loads. At Santa Giustina, sewage sludge receives anaerobic digestion and mechanic dehydration treatment. Heat is also recovered during the treatment process (Gruppo HERA, 2023).

2.2. The anthropogenic P cycle and system MFA archetypes

To develop a model that is comparable to the existing literature on P flow analysis (PFA), we referred to a system archetype, which is commonly used in systemic approaches when specific patterns are persistent and suitable for the elaboration of new models. More specifically, two PFA studies from the literature were used as archetypes for the modelling of the system comprehending the municipalities served by the WWTP of Santa Giustina. The first model was developed by van Dijk et al. to assess the aggregate P flow from the EU, accounting for the imports and losses of P at the continental level (van Dijk et al., 2016). The second model was developed by Koppelaar and Weikard to quantify the global P flows from its extraction until its landfill deposition. Both models present similarities but contain different boundaries and processes (Koppelaar and Weikard, 2013).

Van Dijk et al. makes the distinction between the P flows that occur in a geological timescale from the cycles occurring at a human timescale and mainly because of the human management of this resource. In their study, where the flows of P from the EU Member States were quantified, they took out of the boundaries the extraction and mining activities, since virtually all the mined P that is sourced to the member states occurs outside the EU. Therefore, these authors considered the following finished goods as the flows entering the systems: mineral fertilizers, animal feed additives, food P additives, and detergents (van Dijk et al., 2016).

The urban-agricultural system can be considered as an open system, in which material exchange with the outside environment occurs in different proportions. Moreover, there is an interaction between the anthropogenic and geologic cycles, which differ in timescales and magnitude of flows. Once P is applied to soils, there are four main pathways it can follow. A first pathway is the accumulation of P in the soil, since not all P is taken up by the crops, grasses, and plants in general (van Dijk et al., 2016). A second pathway is the entrance into natural subsystems, in which P circulates from the soil to crops, and returns to the soil when the crop residues degrade in the soil and bacteria decomposes the molecules containing P (Rattan and Stewart, 2017). If crops and grass are used to feed livestock, then P follows a slightly larger cycle (third pathway), in which P is consumed by the animals and later excreted (Smits and Woltjer, 2018). If crops and livestock destiny is human consumption, P leaves the agricultural subsystem and does not directly flow again into the soil (fourth pathway). Finally, natural runoff and erosion make soils lose their P availability.

The following stage covers food processing and non-food commodities production. Food waste can either return a fraction of P into

the agricultural system if used as a source of fertilizer for soils or it can end in landfills depending on the waste treatment procedures that take place in the delimited system (Smits et al., 2018).

Food is consumed by humans after being processed and traded. In this stage, food waste can be generated or discharged in excreta. Excreta is assumed to enter wastewater systems which can be diverse in their procedures; hence varying the fate of P, which could be either recovered (Scholz et al., 2014) or released into marine ecosystems (Smits et al., 2018). Van Dijk et al. include returning flows of P after consumption that enter again the food production, but also quantifies the P that is lost without considering the waste treatment practices (van Dijk et al., 2016).

The generic system diagram developed for P flows and stocks in this study is shown in Fig. 1.

2.3. Data collection and main assumptions

MFA may be very intensive in data collection, for which the use of complementary statistics and accounting approaches (e.g., topdown, bottom-up, Müller et al., 2014) are often necessary to address the complexity of determining a material flows and stocks in an anthropogenic system. Common data sources include databases, reports, and scientific literature or by taking direct or indirect measurements on site (Brunner and Rechberger, 2005).

For the present MFA, data were gathered to quantify the annual metabolism of P withing the selected municipalities of Rimini and complemented with literature sources including factsheets from the European Sustainable Phosphorus Platform (ESPP, 2019). In particular, the data covered the application of fertilizers in the agricultural soils of the province (Table 1), the agricultural and animal food production (Camera di commercio della Romagna-Forli-Cesena e Rimini, 2020. Agricoltura 2019. Le statistiche dell'agricoltura in provincia di Rimini. Camera di commercio della Romagna-Forli-Cesena e Rimini, 1-32.) (Table S4 in the SI), the food consumption based on an average Italian diet (Sette et al., 2011) (Tables S5–S6 in the SI), the P concentration of the influents and effluents of the WWTP of Santa Giustina (European Environment Agency, 2020), and the fate of P in agricultural fields and the local waste management systems (ARPA - Agenzia Prevenzione Ambiente Energia Emilia-Romagna, 2021; van Dijk et al., 2016; ISPRA, 2015). Most data were only available at municipality level: thus, reasonable estimates were computed by scaling the magnitude of the provincial flow with the proportional population size of the chosen municipalities (Admin Stat Italia, 2021). This assumption implies that the total provincial flow is equally distributed along each of the municipalities that conform the Province of Rimini.

The U.S. Department of Agriculture provides a comprehensive database (U.S. Department of Agriculture, 2020) containing the mineral content of diverse foods. To obtain the annual P content in all the harvested crops, the harvest volume of each crop type was multiplied by its P content in its raw form. Manure and crop residuals were assumed to be reutilized as organic fertilizers in their entirety. The associated content of P in organic waste was calculated by taking the fraction of organic waste that was used in the MFA model by Koppelaar and Weikard (2013).

Sette et al. conducted the third national food consumption survey in Italy to obtain the average intakes of micro- and macronutrients in average Italian diets. The results were designed to represent the total population at a national level and include the P intake in males and females of different group ages (Sette et al., 2011).

Under the Urban Wastewater Treatment Directive (91/271/EEC) Member States are required to report information on their wastewater treatment infrastructure and the influent and effluents that WWTPs process. This report, available at the European Environmental Agency site, included the incoming and discharged P concentrations in the effluent of Santa Giustina, as well as the load entering the treatment facilities. P content in superficial waters is monitored throughout the year by the Regional Agency for

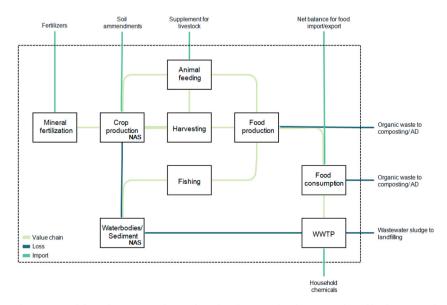


Fig. 1. System diagram with processes and flows characterizing the P cycle in the urban-agricultural system conformed by the municipalities that are served by the wastewater treatment plant (WWTP) of Santa Giustina in the Province of Rimini.

Table 1

Summary of distributed fertilizers in the province of Rimini and their phosphoric anhydride content. Based on (ISTAT, 2021).

Type of fertilizer	Distributed Fertilizer		P ₄ O ₁₀ content	
	tons	%	tons	%
mineral, compound, organic and organic-mineral fertilizers	7834	40%	554	96%
thereof: mineral	2020	10%	54	9%
thereof: compound	424	2%	180	31%
thereof: organic	3261	17%	26	5%
thereof: organic-mineral	2117	11%	292	50%
Amendments	9370	48%	25	4%
soil correctives	0	0%	0	0%
crop substrates	2158	11%	0	0%
specific action products	76	0%	0	0%
Total	19,438	100%	579	100%

Prevention, Environment and Energy of Emilia-Romagna. A study by Santolini and Morri provided the average annual P concentrations in the Marecchia River (Santolini and Morri, 2017).

Waste and losses occur along the entire P metabolism chain. However, food residuals were only considered to happen in the food production stage, disregarding the magnitude of P that is lost or sent to the solid waste management system at the local food supply chain. To estimate the amount of P that is discarded as household organic waste after food consumption and put into the solid waste management system, data reported by the Regional Agency for Prevention, Environment and Energy of Emilia-Romagna were used (ARPA, 2020). The fraction of P contained in organic waste was calculated after the study by (Tuszinska et al., 2021), who measured the amount of P compounds in food waste samples from agricultural and municipal biogas plants.

Given the variability of sources, the level of aggregation in which data is available and their diverse quality, three additional inflows were added at distinct stages of the model to match mass balance constraints. The first one was calculated to satisfy the nutritional needs of the animal feed. Food supplements for animals are included in other MFAs as animal diets require additional sources of P (van Dijk et al., 2016; Koppelaar and Weikard, 2013). Another aspect that was simplified in the model was the net balance of food imports and exports. Since this trade of goods at an aggregate level can be seen as a simple exchange of P, the inflow was calculated to fulfill the nutritional requirements of the population based on their average annual P intake. The final inflow that was calculated to cope with the inflow/outflow mismatches was the P content in non-edible products used at households.

2.4. Uncertainty analysis

Exogenous values employed in MFA models are generally obtained from different sources that used different methodologies, which implies that data come in different formats and qualities. In this view, data used in MFA are cross-disciplinary and highly heterogenic and, as such, subjected to different levels of uncertainty and limited in accuracy (Allesch and Rechberger, 2018).

Several approaches based on data classification have been developed to account for uncertainties in the data (Allesch and Rechberger, 2018). Hedbrant and Sörme developed a method of asymmetric intervals based on the assignment of uncertainty factors for different uncertainty levels. This approach classifies uncertainty levels from 1 to 5 to societal data in environmental research, when conditions for statistical treatment are not met (Hedbrant and Sörme, 2000).

Likewise, Laner et al. (2014) developed a method based on symmetric intervals. They used probability distributions to represent uncertain values, assuming that for most values, there will be a true value within the intervals, which in absence of samples, can be assigned by an expert judgement (Allesch and Rechberger, 2018). Weidema and Wesnaes proposed a Pedrigree Matrix that has been widely used in MFA (Allesch and Rechberger, 2018). The matrix highlights the data quality and the data collection strategy as

Level	UF	Source	Geographical Correlation	Example	Symmetrical interval
0	*/1	General Value	_	P Molecular weight	±0%
1	*/1.1	Official Statistics, appropriate scientific literature	Data from area under study and or average data from larger area in which the area under study is included	Data from regional agencies (e.g., Emilia- Romagna)	$\pm 10\%$
2	*/1.25	Official Statistics, appropriate scientific literature	Data from area with similar production conditions.	Data from European Environmental Agency.	$\pm 25\%$
3	*/1.33	Non-official statistics, presentations	Data from distinctly different area.	P content of organic wastes. Data from U.S. Department of Agriculture and studies using samples from other geographical areas.	±33%
4	*/2	Educated guess, publications without a source.	Data from unknown area or area with distinctly different production conditions.	Mineral fertilizer use in gardens, estimations of transfer coefficients.	±100%

UF: uncertainty factor.

Table 2

parameters to define semiquantitative indication of the reliability, completeness of the data, and temporal, geographical, and technological correlations. Through these five independent data quality indicators, the Pedigree Matrix communicates data limitations that can be associated to uncertainties.

The model developed for this study is based on the uncertainty factors by Hedbrant and Sörme but following symmetric intervals around the magnitude of each input data (Hedbrant and Sörme, 2000). In this way, five levels of uncertainty according to the guidelines were used but adapted to a symmetrical form (Table 2 and Table S7 in the Supporting Information). These five levels of uncertainty define the uncertainties following a simplified version of the Pedigree Matrix (i.e., limited to source reliability and geographical representativeness indicators) from which data were obtained to elaborate the model (Table S7 in the Supporting Information). Further details on equations to account for uncertainty propagation are described in section S3 in the Supporting Information.

3. Results and discussion

3.1. Phosphorous flows and stocks characterization

The MFA model in Fig. 2 displays and quantifies the flows of P in the urban-agricultural system conformed by the municipalities that are served by the WWTP of Santa Giustina. Similarly, Fig. 3 shows each flow with its corresponding uncertainty range. Both figures categorize flows according to their pathways within the system: import, loss, and value chain flows. Annual values are in t of P equivalent. Fig. 4 plots the phosphorous concentration versus medium magnitude for specific waste streams.

Italy has no mineable reserves of phosphate rock. Thus, it relies entirely on P imports and recycling to supply its fields with this nutrient. While no direct information on the total food imports was obtained, a hypothesis to explain the relatively large amount of its magnitude is the low production of animal food originated in the province. Our PFA model shows that about 236 ± 23 t P enter the system annually in form of mineral fertilizers, feed additives for livestock, soil amendments, household chemical products (e.g., detergents) and imported food. The inflow of mineral fertilizers responds to the agricultural activity of the municipalities which mainly produce whole wheat cereal, lettuce, alfalfa, and grapes.

More specifically, 122 ± 12 tons P/year of the total inflow entering the system is driven by the application of fertilizers to agricultural soils. Additional imports include 71 ± 15 t P/year resulting from the net trade balance of finished food products import, 15 ± 14 t P/year from supplemental food additives to livestock, and 20 ± 7 t P/year in detergents and other household chemicals reaching Santa Giustina from houses connected to the wastewater system.

The greater mass flow of P within the system goes from the agricultural soils to the harvested products. The 158 \pm 31 t P/year include crops for both human and livestock consumption. 34 \pm 29 t P/year are estimated to return to the soils as agricultural residues, containing a fraction of the P that is taken up by the crops. Organic fertilizers are also applied in the municipalities (55 \pm 7 t P/year), while 7 \pm 1 t P/year are supplemented by soil amendments produced from digested sewage sludge.

The annual natural runoff of P into waterbodies amounts to about 45 ± 8 t P/year. This flow represents the amount of P that enters the Marecchia River, as past studies have shown that the river effluent had an average P concentration of 0.31 mg/L from 2017 to 2020 (Santolini and Morri, 2017). The mass balance in agricultural soil (i.e., Crop production stage) suggests that there is a net accumulation of 15 ± 23 t P/year.

The model distinguishes between three different sources of P for food production. The main source comes from harvested products,

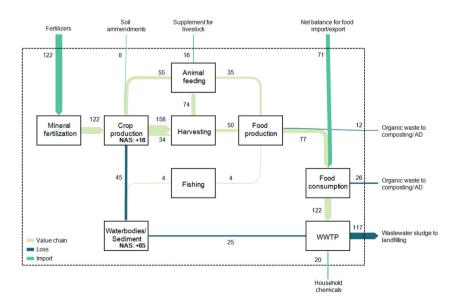


Fig. 2. The P cycle in the urban-agricultural system conformed by the municipalities that are served by the wastewater treatment plant (WWTP) of Santa Giustina in the Province of Rimini. Values are in metric tons (t) of phosphorous contained. NAS: net addition to stock.

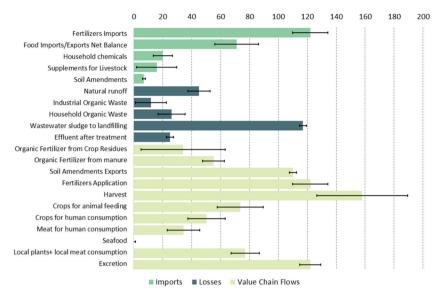


Fig. 3. Flows magnitude and uncertainties. Values are in metric tons (t) of phosphorus contained.

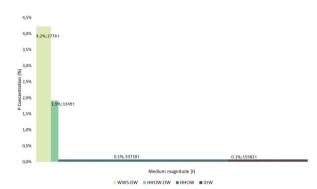


Fig. 4. Phosphorous concentration (%) versus medium magnitude (t) for wastewater sludge, dry weight (WWS-DW); household organic waste, dry weight (HHOW-DW), household organic waste (HHOW), and industrial organic waste (IOW).

intended for human consumption, and resulting in 50 \pm 13 t P/year. Another 34 \pm 11 t P/year come from animal products. The last inflow comes from sea products fished in the Adriatic Sea and commercialized at the Rimini market (4 \pm 1 t P/year). Food scrap and non-edible material are discarded and assumed to leave the system with no further recycling, accounting for 12 \pm 10 t P/year.

A national survey on food consumption habits in Italy suggests that the average P daily intake is around 1200 mg per capita (Sette et al., 2011). Considering the system population throughout the year, 122 ± 7 t P/year are consumed. Since 77 ± 9 t P/year come from local sourced products, an annual P flow of 71 ± 15 t is estimated to come from the food net trade balance. This balance would add all imports and subtract all exports of the food system, filling the lack of statistics related to the trade of foods at province level in terms of mass and list of P-containing products.

According to the 2020 report on Waste Management in Emilia-Romagna, 45,000 t of organic waste are separately collected in the entire Province of Rimini from which 33,700 t correspond to the municipalities included in the system (\sim 75%). A recent study measured an average of 19 ± 1 mg per gram of dry weight (mg/g_{dw}) of P in organic food waste (Tuszynska et al., 2021). The same study reported that dry matter of the organic waste samples was 4% ± 1%. Based on these samples, the P contained in 33,700 t of organic waste ranges between 26 ± 9 t.

The 122 ± 7 t P/year that are consumed by the population and visitors are assumed to be excreted into the sewage system. At this point, the excreted P is mixed with P contained in household chemicals, both conveyed to the WWTP of Santa Giustina and corresponding to about 142 ± 3 t P annually. This quantity represents the recovery P potential that could be achieved at the theoretical 100% efficiency rate in the wastewater treatment facility. In 2021, the current treatment technologies at the site allowed the removal of about 117 ± 2 t P/year from wastewater, which corresponds to a P removal efficiency rate of 82%, in compliance with the EU Directive 91/271/EEC.

Nearly 45% of the sewage sludge produced in the Emilia Romagna region is sent to landfill coverage, while 32% is treated and applied in agricultural soils, 14% is incinerated, and the remaining 9% is recovered for cement production and other products. In

C. Mejia Duque Torres et al.

Rimini, around 7000 t of dry weight of sewage sludge are treated and sent to landfill coverage (ISPRA, 2015).

Finally, the P discharge after water treatment amounts 25 ± 3 t P/year and adds to P leached flow from crop production: the resulting net P addition to stock amounts to 66 ± 8 t P/year and runs off to natural water bodies, as measured by the water quality monitoring station at the Marecchia River, and likely undergoes natural sedimentation once it reaches the Adriatic Sea. This P is assumed to be virtually lost, since the dynamics of P once it enters waterbodies is difficult to predict. More research in this direction is needed. If natural runoff coming from over-fertilized soils is combined with WWTPs discharge points, concentrations of P in surface and groundwaters can increase to above desired levels. Improved agricultural techniques and lower concentrations in water effluents should be promoted by local authorities and other stakeholders to avoid eutrophication events.

Overall, the results suggest that out of the 236 \pm 23 t P/year that enter the Province of Rimini, 81 \pm 21 t P/year are accumulated in the system, and 155 \pm 14 t P/year leave its analytical boundaries via the waste management systems.

3.2. Toward phosphorous circularity in the province of rimini

Eurostat developed the "circular material rate" indicator to monitor the level of circularity within the EU Economy (Eurostat, 2021). This circularity rate is used to measure the contribution of recycled materials to meet the overall material requirements in a system. Applying this metric to our model, a full recovery of the P contained in the wastewater sludge at Santa Giustina would ideally meet 96% of the annual demand of mineral fertilizers in the covered municipalities, confirming WWTPs as hotspots for P recovery (Di Maria and Sisani, 2019; Meng et al., 2019). Moreover, wastewater sludge is the flow with the highest concentration of P, compared to other waste flows as seen in Fig. 4. Notwithstanding this, such a circularity potential for P may remain only theoretical since the digested sludge produced at Santa Giustina is sent to landfill coverage and no further technological application to recover P is applied at today conditions. Hence, the current circularity rates within the system are minimal.

Research by Papa et al. showed that nutrient recovery from sewage sludge is broadly practiced in the majority of WWTPs of Italy. Either by composting or direct land spreading, the destinations of sewage sludge reuse account for 79% in the Italian territory, following a major behavior within the EU where more than 50% of the sludge is reused for agriculture (Papa et al., 2017). In Emilia Romagna, a third of the sewage sludge produced in the regional WWTPs is applied in agricultural soils and composting applications (ISPRA, 2015), suggesting that the region might be implementing actions to recover this resource, while almost the whole amount of wastewater sludge generated at Santa Giustina is landfilled.

However, behind this situation there is not only a problem of non-optimal management of resources, but also a serious principle of prevention. Indeed, current regulatory trends concerning the safety and risk assessment of digested sludge products may pose future challenges to continue with this practice (Egle et al., 2015) and may hinder its implementation in the province of Rimini. The Directive 86/278/EEC regulates the use of sewage sludge for agricultural uses, establishing standards to prevent harmful effects on soil, vegetation, animals, and humans. It defines sludge as (i) the residual from sewage plants that treat domestic or urban wastewaters, or (ii) the residual sludge resulting from septic tanks used for treating sludge. While treated sludge is defined as the sludge that has undergone biological, chemical, or heat treatment. In Emilia-Romagna, the regional norm DGRER 2773/2004 establishes the concentration limits of substances and pathogens in sludge to be applied as soil amendment, ultimately prohibiting sludge application for horticulture and fruit agriculture where products are characteristically close to the terrain and are consumed as raw products. (ISPRA, 2015).

In this context, other end-of-life strategies might define a trend for the near future, as more stringent limits on heavy metals, pathogens, and persistent organic pollutants might be established at European, national, and regional regulations. In particular, incineration could be a preferred pathway for sludge disposal, similarly to what happens in other EU countries such Germany, the Netherlands, and Belgium (Papa et al., 2017).

Thermal treatment of sludge reduces the risk associated with pathogens, viruses, and persistent organic pollutants, and it can be preparatory to an efficient P recovery. In particular, a dewatering process prior to combustion can concentrate 85–90% of the P contained in the incoming sludge (Icardi, 2023). The ability to achieve relatively high extraction rates (i.e., 75–90%) from a dry sludge containing 5–11% of P (Boniardi et al., 2021) gives incineration ash significant potential as a main secondary source of P, although potential issues due to co-dissolution of metals (e.g., As, Cr, Pb) should be carefully evaluated (Li et al., 2017). Assuming similar efficiency rates for P concentration and recovery are achieved at regional incineration plants, the circular material rate index for the system investigated would be around 61–78%.

Other strategies for P recovery could be implemented more locally, involving directly the WWTP in Santa Giustina. Current research to develop scalable and economically feasible technologies to recover P at WWTPs include precipitation and crystallization if P as struvite from upstream or downstream sludge dewatering, P-removal from dewatered sludge through hydrothermal hydrolysis carbonization or thermochemical leaching and phosphate precipitation, and pyrolysis to biochar (not included in EU fertilizing products regulation). Although in several cases these processes have demonstrated to achieve better quality and environmental performance than traditional P-containing products or digestate sludges applied in agricultural fields, several trade-offs still hinder a full scale-up of these technologies so that there is not yet an optimal solution that can obtain profitable high quality P products, with the lowest environmental impacts among the existing technologies. (Remy and Jossa, 2015; Nättorp and Remmen, 2015; Wilken and Kabbe, 2015).

Although economic considerations still hinder the large-scale implementation of these technologies, their competitiveness might increase with the growing of the P market price. Further, better economies of scale could result from the development of dedicated combustion line (i.e., single waste) and centralized systems. One specific barrier that limits the economic potential of these technologies is the market regulations for P recovered products. Special attention must be given to the quality characteristics of the products, their bioavailability, and their compliance with existing regulations for fertilizers, chemical products, and their

characterization as waste or a marketable product.

If favorable technical-economic considerations can determine a quantitative recovery of P through efficient management of waste and residues at the WWTP in Santa Giustina, there might be the possibility of establishing a short supply chain as the availability of secondary P approaches the order of magnitude of P imports into the system and opening business opportunities for local firms to enter the production of P-based fertilizers.

In any case, the achievement of sustainable production and consumption of P cannot ignore a less intensive use of the soil, a reduction in inefficiencies such as food waste, and greater respect for dynamics of biogeochemical cycles. Given the intense agricultural and breeding activity that characterizes the investigated system, the pursuit of such prevention principles could lead to significant benefits in terms of reducing the demand for P and achieving and an ideally balanced circularity in its local anthropogenic cvcle.

4. Conclusions

This study has characterized the P anthropogenic cycle at the local level and evaluated the potential to achieve a greater level of circularity in the Province of Rimini regarding the recovery of P at the WWTP of Santa Giustina. The results demonstrate that the greatest potential for P recovery is embedded into the digested sludge from the WWTP, which would ideally meet up to 96% of the annual demand of mineral fertilizers in the system. However, this flow is currently disposed of by landfilling. Technical, economic, environmental, and regulatory evaluations are ultimately needed to build a positive business case to recover P in the region.

Although the present work could be further improved by reducing data uncertainties arising from the availability of disaggregated economic data of the studied municipalities (including, for instance, more precise data on the actual loads of P in the treated waters with their respective variability along the different seasons of the year and quantifying the flows that were calculated to conform the mass conservation law), our model has characterized P flows and stocks in the Province of Rimini, helping define the current levels of material circularity and provide guidance to decision-makers on the spots where action should be taken to increase resource efficiency.

To this aim, quantitative information provided by the PFA model should be considered as the fundamental basis for follow-up analyses such as life cycle assessment (LCA) and life cycle costing (LCC). Particularly, LCA would enable proper accounting of environmental implications related to P recovery as the results might vary significantly depending on the characteristics of the site (Remy and Jossa, 2015) and be relevant to a set of impact categories such as global warming, fossil resource depletion, eutrophication, and water consumption. In turn, LCC with a social-environmental scope might inform about the environmental impacts of P when released in quantities that surpass the carrying capacity of a given ecosystem. This is the case for areas in which the natural water network is vulnerable to high nutrient concentration levels that can lead to eutrophication. Moreover, it was early highlighted that P is in the list of critical materials for the EU, as it is considered scarce within the territory and most of the extraction of mined P virtually occurs in five countries. This poses a long-term threat for the EU, as P is not exempt from price shocks and geopolitical frictions.

The above-mentioned reasons might be of importance for developing strategies in which P recovery, together with the introduction of safe products, the impulse of food security, and circularity are shown to account for an overall social and environmental benefit. While prevention-oriented technologies could offer effective ways to remove P from the influent waters, a shift into technologies that also promote the recovery of marketable P products might push for higher removal rates, hence increasing the circularity performance of wastewater systems.

Author statement

Conceptualization: FP and LC; Data curation: CMDT, LC; Formal analysis: CMDT; Methodology: FP, LC, and CMDT; Visualization: CMDT, LC; Writing - original draft: CMDT, LC, and FP; Writing - review & editing: CMDT, LC, and FP.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scp.2023.101133.

References

Admin Stat Italia, 2021. Maps, analysis and statistics about the resident population [Online]. https://ugeo.urbistat.com/AdminStat/en/it/demografia/popolazione/ rimini/99/3. May 2023. Allesch, A., Rechberger, H., 2018. Compilation of Uncertainty Approaches and Recommendations for Reporting Data Uncertainty. Minfuture, Wien.

ARPA - Agenzia Prevenzione Ambiente Energia Emilia-Romagna, 2021. La gestione dei rifiuti in Emilia-Romagna. Grafiche Lama S.r.l, Piacenza. Report 2020.

Baroi, A.R., Biswas Chowdhury, R., Bhuson Roy, B., Sujauddin, M., 2020. Sustainability Assessment of Phosphorus in the waste management system of Bangladesh using substance flow analysis. J. Clean. Prod. 273, 14.

Boniardi, G., Turolla, A., Fiameni, L., Gelmi, E., Bontempi, E., Malpei, F., Canziani, R., 2021. Assessment of a simple and replicable procedure for selective phosphorus recovery from sewage sludge ashes by wet chemical extraction and precipitation. Chemosphere 285, 131476.

Brinkmann, T., et al., 2016. Best Available Techniques (BAT) Reference Document for Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector. EUR 28112 EN, Luxembourg.

Brunner, P.H., 2010. Substance flow analysis as a decision support tool for phosphorus management. J. Ind. Ecol. 14 (6), 870-873.

Brunner, P.H., Rechberger, H., 2005. Practical Handbook of Material Flow Analysis, first ed. Lewis Publishers, Boca Raton

Camera di commercio della Romagna-Forli-Cesena e Rimini, 2020. Agricoltura 2019. Le statistiche dell'agricoltura in provincia di Rimini. Camera di commercio della Romagna-Forli-Cesena e Rimini, pp. 1–32.

Centro di ricerca Politiche e Bioeconomia, 2021. L'agricoltura Italiana Conta 2021. CREA, Roma.

Childers, D.L., Corman, J., Mark, E., Elser, J.J., 2011. Sustainability challenges of phosphorus and food: solutions from closing the human phosphorus cycle. Bioscience 61 (2), 117–124.

Ciacci, L., Reck, B.K., Nassar, N., Graedel, T.E., 2015. Lost by design. Environ. Sci. Technol. 49 (16), 9443–9451.

Cordell, D., Drangert, J.-O., Stuart, W., 2009. The story of Phosphorus: global food security and food for thought. Global Environ. Change 19 (2), 292–305. Egle, L., Rechberger, H., Zessner, M., 2015. Overview and description of technologies for recovering phosphorus from municipal wastewater. Resour. Conserv. Recycl. 105, 325–346.

Di Maria, F., Sisani, F., 2019. A sustainability assessment for use on land or wastewater treatment of the digestate from bio-waste. Waste Manage. 87, 741–750. Egle, L., et al., 2014. The Austrian P budgetas a basis for resource optimization. Resour. Conserv. Recycl. 83, 152–162.

Ellen McArthur Foundation, 2013. Towards the Circular Economy. Opportunities for the Consumer Good Sector. Ellen McArthur Foundation.

European Commision, 2023. Implementing and delegated acts - Taxonomy Regulation [Online]. http://ec.europa.eu/finance/docs/level-2-measures/taxonomy-regulation-delegated-act-2022-environmental-annex-2 en.pdf.

European Commission, 2020. Study on the EU's List of Critical Raw Materials. Final Report., Brussels: s.n.

European Environment Agency, 2020. Waterbase - UWWTD: urban waste water treatment directive - reported data [Online]. https://www.eea.europa.eu/data-andmaps/data/waterbase-uwwtd-urban-waste-water-treatment-directive-7. May 2023.

European Sustainable Phosphorus Platform (ESPP), 2019. ESPP phosphorus fact sheet [Online]. https://www.phosphorusplatform.eu/home2. May 2023. eurostat, 2021a. Circular Economy - material flows [Online] Available at: https://ec.europa.eu/eurostat/statistics-explained/index.php?title=Circular_economy_-

material_flows#Description_of_flows_and_nodes_of_the_Sankey_diagram. May 2023. Gruppo, H.E.R.A.. Gli impianti di Hera e l'*uso efficiente delle risorse idriche* [Online]. https://www.gruppohera.it/gruppo/attivita/acqua/i-nostri-impianti. May 2023. Hedbrant, J., Sörme, L., 2000. Data Vagueness and Uncertainties in Urban Heavy-Metal Data Collection. Linköping: Department of Water and Environmental Studies.

Linköping University.

Houssini, K., et al., 2023. Measuring anthropogenic phosphorus cycles to promote resource recovery. Resour. Pol. 81, 11.

ISPRA, 2015. Uso dei fanghi di depurazione in agricoltura: attivita di controllo e vigilanza sul territorio. Istituto Superiore per la Protezione e la Ricerca Ambientale, Roma.

ISTAT - Istituto Nazionale di Statistica, 2021. Fertilizzanti distribuiti - prov [Online]. http://dati.istat.it/index.aspx?queryid=23961. May 2023.

Karunanithi, R., et al., 2016. Phosphorus recovery from wastes. In: Environmental Materials And Waste. Resource Recovery And Prevention.. s.L. Academic Press, pp. 687–705.

Koppelaar, R., Weikard, H., 2013. Assessing phosphate rock depletionand phosphorus recycling options. Global Environ. Change 23, 1454–1466.

Laner, D., Rechberger, H., Astrup, T., 2014. Systematic evaluation of uncertainty in material flow analysis. J. Ind. Ecol. 18, 859–870.

McCullough, E., Nassaer, N.T., 2017. Assessment of critical minerals: updated application of an early-warning screening methodology. Mineral Economics 30, 257–272.

Meng, X., Huang, Q., Xu, J., Gao, H., Yan, J., 2019. A review of phosphorus recovery from different thermal treatment products of sewage sludge. Waste Dispos. Sustain. Energy 1, 99–115.

Müller, E., Hilty, M., Schluep, M., Faulstisch, M., 2014. Modeling Metal Stocks and Flows: A Review of Dynamic Material Flow Analysis Methods, vol. 48. Environmental Science and Technology, pp. 2102–2113.

Nättorp, A., Remmen, K., 2015. Report on LLC of European P recovery processes. In: Sustainable sewage sludge management fostering phosphorus recovery and energy efficiency, p. 57. Muttenz.

Panagos, P., et al., 2022. Improving the phosphorus budget of European agricultural soils. Science of the Environment 853, 17.

Papa, M., Foladori, P., Guglielmi, L., Bertanza, G., 2017. How far are we from closing the loop of sewage resource recovery? A real picture of municipal wastewater treatment plants in Italy. J. Environ. Manag. 198, 9–15.

Papangelou, A., Achten, W.M., Mathijs, E., 2020. Phosphorus and energy flows through the food system of Brussels Capital Region. Resour. Conserv. Recycl. 156, 12. Presidenza dei Consiglio dei Ministri, 2021. Implementation Action Plan (2020-2025) for the Italian Bioeconomy Strategy, s.l.: Comitato Nazionale per la Biosicurezza. le Biotechnologie e le Scienze della vita.

Rattan, L., Stewart, B., 2017. Soil Phosphorus, first ed. Taylor and Francis Group, Boca Raton.

Reike, D., Vermeulen, W., Sjors, W., 2018. The circular economy: new or refurbished as CE3.0? Exploring controversies in the conceptualization of the circular economy through a focus on history and resource value retention options. Resour. Conserv. Recycl. 135, 246–264.

Remy, C., Jossa, P., 2015. Deliverable D 9.2 Life Cycle Assessmentof selected processes for P recovery from sewage sludge, sludge liquor or ash. In: KWB (Ed.), Sustainable Sewage Sludge Management Fostering Phosphporus Recovery and Energy Efficiency. s.n., Berlin, p. 86.

Santolini, R., Morri, E., 2017. Valutazione del rischio ambientali da fonti inquinanti puntiali e diffuse, Forli: Romagna Acque. Societa delle Fonti.

Scholz, R.W., et al., 2014. Sustainable Phosphorus Management. A Global Transdisciplinary Roadmap, 1 ed. Springer Netherlands, Dordrecht.

Sena, M., Seib, M., Noguera, D.R., Hicks, A., 2021. Environmental Impacts of phosphorus recovery through struvite precipitation in wastewater treatment. J. Clean. Prod. 280.

Servizio Statistica e Sistemi Informativi Geografici, 2019. Rapporto annuale sul movimento turistico e la consistenza ricettiva alberghiera e complementare in Emilia Romagna. Servizio Statistica e Sistemi Informativi Geografici, Bologna, 2018.

Sette, S., et al., 2011. The third Italian national food consumption survey, INRAN-SCAI 2005-06 Part1: nutrient intakes in Italy. Nutr. Metabol. Cardiovasc. Dis. 21, 922–932.

Treadwell, J.L., Clark, O.G., Bennett, E.M., 2018. Dynamic simulation of phosphorus flows through Montreal's food and waste systems. Resour. Conserv. Recycl. 131, 122–133.

Tuszinska, A., Czerwionka, K., Obarska-Pempkowiak, H., 2021. Phosphorus concentration and availability in raw organic waste and post fermentation products. J. Environ. Manag. 278.

U.S Department of Agriculture, 2020. Fooddata Central Download Data [Online]. https://fdc.nal.usda.gov/download-datasets.html. May 2023.

van Dijk, K.C., Lesschen, J.P., Oenema, O., 2016. Phosphorus flows and balances of the European union member states. Sci. Total Environ. 542, 1078–1093. Wang, J., Qi, Z., Bennett, E.M., 2022. Changes in Canada's phosphorus cycle 1961–2018: surpluses. Global Biochemical Cycles 36.

Wilken, V., Kabbe, C., 2015. Quantification of nutritional value and toxic effects of P recovery product. In: Sustainable Sewage Sludge Management Fostering Phosphorus Recovery and Energy Efficiency. s.n., Berlin, p. 20.

Zhu, F., Kendir Cakmar, E., Cetecioglu, Z., 2023. Phosphorus recovery for circular Economy: application potential of feasible. Chem. Eng. J. 454, 15.

Zoboli, O., Laner, D., Zessner, M., Rechberger, H., 2015. Added values of time series in material flow analysis. The Austrian phosphorus budget from 1990 to 2011. J. Ind. Ecol. 20, 1334–1348. Icardi, M., 2023. Recupero del fosforo: problematiche e progetti di ricerca. La Chimica e la Società, il Blog della SCI. In. https://ilblogdellasci.wordpress.com/2023/01/08/recupero-del-fosforo-problematiche-e-progetti-di-ricerca/ (Accessed May 2023).
Li, J.-s., Tsang, D.C.W., Wang, Q. ming, Fang, L., Xue, Q., Poon, C.S. 2017. Fate of metals before and after chemical extraction of incinerated sewage sludge ash. Chemosphere 186, 350-359.

Smits, M.J.W., Wolfer, G.B., Luesink, H.H., Beekman, V., de Koeijer, T.J., Daatselaar, C.H.G., Duin, L., 2018. Phosphorus Recycling from manure – A Case Study on the Circular Economy: Work package 4. EU. https://circular-impacts.eu/sites/default/files/D4.5_Case-Study-Nutrient-Recycling_FINAL.pdf (Accessed May 2023).