UNIVERSITÀ CATTOLICA DEL SACRO CUORE
Sede di Piacenza

Dottorato di ricerca per il Sistema Agro-alimentare
Ph.D. in Agro-Food System

Cycle XXXV
S.S.D. AGR/02

Towards an efficient management of livestock slurries in intensive agro-ecosystems: insights on N loss pathways, trade-offs, and mitigation strategies.

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Matriculation n:

4915013

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Content

SUMMARY

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Slurries and manures have always represented a valuable source of fertility as soil improvers and fertilizers for Agriculture. However, with intensification processes related to growing population and industrialization, animal husbandry has become increasingly impacting on the agroecosystem, with correct slurries management as a key point to address, from storage to land application, to avoid undesirable nutrients losses and side effects on the environment.

Nitrogen (N) is at the same time the most important crop yield-limiting factor (together with water) and the most overused plant macronutrient, especially in the form of chemical fertilizers, which can be partially, or totally, as for Organic Farming, replaced with manures and slurries. However, the adoption of sustainable management strategies for slurries and manures that can improve their fertilizing value, should necessarily come with a reduction in the leakage of N through reactive forms (Nr) that represent not only a loss of nutrient value, but also a threaten to human and environmental health.

Between the most impacting Nr losses from manures and slurries application to agricultural land, there are ammonia (NH_3) volatilizations, nitrate (NO_3^-) leaching and nitrous oxide (N_2O) emissions. Rarely, those Nr loss pathways have been simultaneously analysed. However, there is major need to gain a comprehensive insight of the issue to safeguard as much as possible the N budget from soil, without unnecessarily increasing exogenous N supplies. Moreover, a comprehensive approach may foster understanding of better strategies to avoid pollution swapping between different Nr loss pathways in different agroecosystems. In addition, reduction of N losses should translate in higher Nitrogen Use Efficiencies (NUE) by cash crops.

Specific objectives of this thesis are: (i) to identify distribution strategies of livestock slurry that minimize Nr losses, while enhancing NUE, across various intensive agro-ecosystems, including the permanent grasslands and the maize cultivations in the Italian Po valley; (ii) to test Nr losses mitigation strategies based on sustainable agriculture practices, including cover crops, and innovative slurry treatment and distribution strategies (i.e., fertigation); (iii) to assess the impact of these strategies on three main Nr loss pathways, namely NH_3 volatilization, NO_3^- leaching and N_2O emissions.

The thesis has 3 research chapters, next to a general introduction (Chapter 1) and a general discussion (Chapter 5).

In Chapter 2, we tested the effect of slurry application timing (autumn *vs.* winter *vs.* spring) and method (injection *vs.* broadcasting) and their interactions on N_2O emissions, NH_3 volatilization

and NO_3^- leaching, as well as on plant N uptake in a permanent grassland of Po valley. We found that autumn application increased NO_3^--N leaching by 119-128% compared to winter and spring due to 63% higher rainfall following application. On average, autumn application reduced plant N uptake by 26%. N_2O-N emissions after winter slurry application were 64% and 80% higher than after spring or autumn applications, respectively. Slurry application method had no effect on NO_3^- leaching. Slurry injection led to 63% higher N_2O emissions compared with broadcast application. Slurry injection decreased NH_3 volatilization only in autumn when the soil was relatively dry before application, but not in winter or spring when the soil was wet. Changes in slurry application timing led to variations in total N losses of up to 146%, and application method of up to 19%, highlighting the great potential of slurry application practices to steer an efficient N management. Overall, autumn application should be avoided to promote more sustainable grassland production; however, if slurry must be applied in autumn, injection should be recommended to reduce NH_3 volatilization.

In Chapter 3, we tested two application methods (i.e., surface broadcasting, BDC; and shallow injection, INJ) of the liquid fraction of separated co-digested cattle slurry (DLF), combined with different winter cover crop options (CCs, i.e., rye, white mustard or bare fallow), at maize pre-sowing. Later, side-dressing with urea was required to fulfil maize N-requirements. We tested treatment effects on yield, N-uptake, N-use efficiency parameters, and N-losses in the form of N_2O emissions and NO_3^- leaching. Cover crops development and biomass production was strongly affected by their contrasting frost tolerance, with spring-regrowth for rye, while mustard was winter killed. After the cover crops, injection of DLF increased N_2O emissions significantly compared with BDC (emission factor of 2.69 *vs.* 1.66%). Nitrous oxide emissions accounted for a small part (11-13%) of the overall yield-scaled N losses (0.46 - 0.97 kg N Mg grain^{-1}). The adoption of CCs reduced fall NO_3^- leaching, being 51% and 64% lower for mustard and rye than under bare soil. In addition, rye reduced NO_3^- leaching during spring and summer after termination by promoting N immobilization, thus leading to -57% lower annual leaching losses compared to mustard. DLF application method modified N-loss pathways, but not the cumulative yield-scaled N losses.

In Chapter 4, we tested the effectiveness of slurry microfiltration and reuse via fertigation as a sustainable technique for maize fertilization under Organic Farming (OF). We compared in a field experiment three different strategies: (i) applying the entire slurry distribution through surface broadcast before sowing as reference OF fertilization ("Ante" treatment, or "A"), (ii) applying 50% of the slurry through pre-sowing broadcast and the remaining 50% through fertigation as side-dressing ("Ante+Post" treatment, or "A+P"), and (iii) applying 100% of the slurry as side dressing via fertigation ("Post" treatment, or "P"). Compared to "A", the cumulative N losses were reduced when fertigation was employed, with reductions of 38% under "A+P" and 58% under "P".

Furthermore, NH_3 volatilization was decreased by 43% and 71% under "A+P" and "P", respectively. N_2O emissions under "A+P" and "P" were 30% and 37% lower than under "A", respectively. Lastly, NO_3^- leaching was significantly reduced by 56% in the "P" treatment. Overall, while the "P" strategy appeared to be the most effective in reducing N losses, the "A+P" strategy achieved slightly higher grain production (12.6 Mg ha^{-1}) and NUE (36.2 kg grain kg^{-1} N supply) than "P" strategy (11.0 Mg ha^{-1} and 31.2 kg grain kg^{-1} N supply). These results were primarily attributed to the improved synchronization between N supply and maize N requirements, emphasizing the critical timing of slurry application before sowing.

To resume, main conclusions of this PhD thesis are as follows:

i. Reactive N loss pathways are variably affected by environmental and climatic conditions: high precipitations in autumn can favor NO_3^- leaching; large N_2O emissions may occur in winter also with low temperatures and low N uptake by crops and NH_3 volatilization can increase with increasing temperatures in spring (Chapter 2);

ii. Slurry surface broadcast is confirmed to significantly increase NH_3 losses (Chapters 2, 3 and 4);

iii. While shallow injection of slurries can significantly abate NH_3 volatilizations compared to surface broadcast, there is a concrete risk of pollution swapping with increased N_2O emissions. On the other hand, NO_3^- leaching seems not to be affected by this technique, compared to surface broadcast (Chapters 2 and 3);

iv. Slurry injection tools (i.e., discs) may damage grassland swards with partial losses on yield (Chapter 2);

v. Agricultural practices aimed to minimize some targeted N losses, like catch crops on NO_3^- leaching, should be thoroughly managed, since their positive role should not be at the expense of other positive effects: in this regard, careful attention should be driven to correct management of cover crops' residue that may represent both an advantage and a problem for Nr losses (Chapter 3);

vi. Fertigation may be a valuable option to synchronize N supplies from slurries with crops N requirements, thus attaining better results for Nitrogen Use Efficiency, especially for high N demanding crops, like maize (Chapter 4).

CHAPTER 1.

General introduction

1.1 The role of N in Agriculture: state of the art and issues

In 2019, Agriculture, together with Forestry and Other Land Use (AFOLU) contributed to 22% of global GHG emissions and seems responsible for a large proportion of global N pollution (Gu et al., 2023). As a trade-off, global climate change is affecting food and water security, thus also hindering UNs' Sustainable Development Goals (IPCC, 2023). Moreover, the threshold of +1.5 °C from pre-industrial age will be likely reached and overridden in the near term, thus involving adverse and possible critical consequences for agriculture and food production (IPCC, 2023). For those reasons Cropland is at a crossroads, and Research must propose solutions to this potential conflict between food production and climate and land protection.

Among all, nitrogen (N) is the plant nutrient which is more often overused (Gu et al., 2023; Wang and Li, 2019), with consequent waste, and possibly leading to "reactive" forms (Nr), that are biologically, radiatively, and photochemically active (Galloway et al., 1995): those include nitrous oxide (N_2O), ammonia (NH_3) and nitrate (NO_3^-), between the most impacting on climate change, soil and water quality and human health (Nieder and Benbi, 2022). Moreover, these losses pose severe issues to N use efficiency (NUE) and must be carefully curbed in the light of new European Green Deal's policies, like the "Farm to Fork strategy" and the "Zero Pollution action plan". In fact, these pose ambitious milestones for the European agriculture, including a 20% reduction in the use of fertilizers and a 50% abatement of nutrient losses by 2030, compared to 2012-2015 (European Commission, 2019), while promoting agro-ecosistemic services of soil and water bodies to balance those reductions.

1.2 Nitrogen fertilizing value of liquid dairy manures

Currently, Haber-Bosch process, that enables NH_3 production and related fertilizers (urea, mainly), contributes to around 1.2% of global CO_2 anthropogenic emissions (Smith et al., 2020), thus urgently calling for its amelioration in the NH_3 synthesis processes and integration/substitution with Nature-based alternatives to synthetic-N fertilizers (Rosa and Gabrielli, 2023). Those may include organic amendments and livestock excreta, like solid manures and liquid slurries (Ren et al., 2022; Zilio et al., 2023).

In Italy, Po Plain is the largest milk and cheese production district with the highest number of dairy farms (Battini et al., 2016). This leads to two main consequences: the need for sufficient land area dedicated to crops for animal feeding, and a vast production of effluents. The two largest PDO

(Protected Designation of Origin) cheeses of the area, namely Parmigiano Reggiano and Grana Padano, mainly rely for their production on grasslands and forage maize, respectively (Battini et al., 2016) and, in this respect, manures (solid) and slurries (with low dry matter content), provided correct management, can represent a valuable source of fertility for that forage crops (Hunt et al., 2019; Zavattaro et al., 2012). This PhD thesis will discuss mainly around slurries: solid manure is not within the scope of the present work.

Slurries composition is highly variable (Marino et al., 2008) and these differences are attributed to several factors, like animal diet, housing system (bed system, cleaning system, etc.), storage management (lagoons, closed *vs*. opened sewage tanks, etc.), etc. (Martínez-Suller et al., 2008). Furthermore, several treatments of these matrices bring to different fractions with different properties: anaerobic digestion (and co-digestion), solid-liquid separation and microfiltration, are just a part of the possibilities (Cavalli et al., 2016; Righi Ricco et al., 2021; Risberg et al., 2017).

The production of bio-methane through the anaerobic digestion of livestock manures (alone, or co-fermented with bioenergy crops) has reached remarkable momentum since the need for alternative energy sources while improving waste management (Lamolinara et al., 2022). Generally, digestates have a higher proportion of ammoniacal N ($NH_3 + NH_4^+$, usually referred to as TAN, Total Ammoniacal Nitrogen), a lower dry matter content, and a lower C to N ratio compared to the undigested substrates (Cavalli et al., 2017; Risberg et al., 2017), which makes them particularly suitable for crop fertilization (Grillo et al., 2021).

Furthermore, solid-liquid separation may be adopted either on raw slurries or downstream their (co)digestion through several types of presses (screw) or other mechanical devices (Hjorth et al., 2011). The solid fraction, easier to manage, can be further processed (e.g., by composting) or kept as it is and mainly adopted as soil improver (Egene et al., 2021; Peters and Jensen, 2011; Vico et al., 2020). On the other hand, liquid fractions has been pointed to have greater fertilizer replacement value compared to untreated slurries, since their higher TAN fraction has been identified as the most readily available in the near term (first year after manure application), compared to the small contribution from mineralization of organic N that tends to increase with subsequent applications over the years (Bechini and Marino, 2009; Cavalli et al., 2016, 2014).

Further available step to refine the liquid fraction of manures are micro- (retains solid particles between 25 and 0.1 µm), ultra- (200 - 5 nm), nano-filtration (400 - 200 Dalton) and inverted osmosis (retains particles below 200 Dalton) (Finzi et al., 2021; Provolo and Perazzolo, 2016). These processes (mainly microfiltration) can be successfully adopted to rise the fertiliser value of digestates and slurries with fertigation that enables fractional application of nutrients with water to crops, with higher degree of synchronization with their requirements, also reducing wastages (Ardenti et al., 2022; Maris et al., 2015). In fact, while synthetic fertilisers completely dissolve in irrigation water, slurries may come with suspended solids with a high particle size that can clog nozzles in driplines (130-200 µm) or pivot (1.6-10 mm) systems (Finzi et al., 2021; Guido et al., 2020), thus adequate filtration, flow rates (0.8–7.1 $m^3 h^{-1}$) and dilution (4–10%) are required (Finzi et al., 2021).

1.2.1 Nitrogen losses after dairy slurries application to agricultural land

Notwithstanding the remarkable value of manures as soil improvers and organic fertilizers, at the time of application, if not correctly managed, manure-derived N may be lost through a wide range of forms: between the most impacting are nitrate laching towards groundwater, leading to eutrophication and non-potable water supplies (Wang and Li, 2019); ammonia volatilization, which is associated to fine particulate matter formation ($PM_{2.5}$) threatening human health (Wyer et al., 2022) and to soil acidification and water eutrophication (Ti et al., 2019); and emissions of nitrous oxide, a strong greenhouse gas (GHG) with a Global Warming Potential (GWP) 298 times higher than CO_2 on 100 years base (Vallero, 2019).

Furthermore, these losses represent a wastage of valuable fertilizing potential and sustainment for crop production. Thus, is of outmost importance to identify techniques to save N and maximize its conversion into food and feed by rising crops' Nitrogen Use Efficiency (Weih et al., 2018; Yu et al., 2022). Moreover, over the years, this need has led to a vast body of legislation that regulates the use of livestock slurry, from storage to field application: a synthetic review of the current legislation in EU can be find in Köninger et al. (2021).

1.2.1.1 Nitrate leaching

Nitrate leaching and runoff are considered the main N-loss pathways accounting for 6.7-19.0 % of applied N in cultivated agricultural lands, with consequent losses of fertilizing potential and degradation of water resources, both superficial and belowground (Wang and Li, 2019).

Leaching occurs mainly after accumulation of NO_3^- in dry periods and subsequent downward movement below root zone following precipitations and irrigations (Wang and Li, 2019) and, generally, during periods with high drainage rates (Hansen et al., 2019). Besides soil water content and irrigation rates, main soil variables related to nitrate losses have been identified in texture, and structure, with coarse textured soils being more prone to leaching (Askegaard et al., 2005). In relation to period of the year, autumn is usually identified as the more prone to leaching losses (Askegaard et al., 2011). In relation to cultivated crops, NO_3^- leaching has been reported as usually lower under grasslands than other annual cultures (Wang and Li, 2019) thanks to their deep expanding rooting apparatus that can more effectively uptake nitrate (Franzluebbers et al., 2014) and to the permanent soil cover that uptakes N also during fall periods. In fact, leaching risk is maximized under bare soil conditions (Thorup-Kristensen et al., 2003) and in late summer or autumn, when synchronization between crops N requirements and mineralization of organic N is more difficult, making it as the most critical period for manure distribution (Askegaard et al., 2011).

In their review, Kirchmann and Bergström (2001) found no clear indication of manures-derived N as being more prone to leaching, compared to mineral fertilizers; thus, the tendency in NO_3^- leaching after solid manures and slurries application to agricultural land could be mainly related to environmental and management variables than to these organic fertilizers *per se*. For these reasons a vast body of law around improvement of slurries and manure management has been developed in years. In the European Union, the 91/676/EEC Directive, best known as “Nitrate Directive” represents the most critical regulation for manure management: it required to EU’s member states the identification of Nitrate Vulnerable Zones where N coming from organic sources must be kept within the limit of 170 kg ha^{-1} y^{-1}, and the identification of Good Agricultural Practices to reduce environmental risks, e.g. by limiting time of the year for application, adopting good storage practices and application techniques (Köninger et al., 2021).

1.2.1.2 Ammonia volatilization

Agriculture is responsible for around 81% of global NH_3 emissions, thus representing the main source (Wyer et al., 2022). Mechanisms leading to NH_3 volatilization from manures application to field encompass both chemical and physical mechanisms, and extensive explanations of those have been reported by several publications (Huijsmans et al., 2003, 2001; Sommer et al., 2006, 2003; Sommer and Hutchings, 2001): slurry dry matter content (DM), total ammoniacal nitrogen (TAN), method of application and their interaction have been recently pointed between the most relevant drivers (van der Weerden et al., 2023).

Updated emission factors for NH_3 (cumulative NH_3-N loss as a proportion of total N applied in the manure) for cattle manure and slurry surface broadcast in temperate wet climates, can range between 0.03 and 0.24 kg NH_3-N kg^{-1} of total applied N, respectively (van der Weerden et al., 2021).

The National Emission Ceiling (NEC) Directive 2016/2284/EU has set the ambitious target of 19% reduction in NH_3 emissions from all EU countries by 2030 relative to 2005: strategies adopted to achieve that mitigation commitment must be carefully calibrated to avoid pollution swapping between NH_3 and other N-loss pathways, like N_2O emissions (Emmerling et al., 2020; Zhang et al., 2022) or NO_3^- leaching (Powell et al., 2011).

1.2.1.3 Nitrous oxide emissions

Agriculture is globally responsible for the vast majority of N_2O emissions (75%), with manures application to grasslands (22%) and synthetic fertilizers (18%) as main global sources (Velthof and Rietra, 2018). Manures contain three essential elements for N_2O emissions, namely N, C and water (Chadwick et al., 2011). For this reason, careful attention must be applied to their whole management continuum, from livestock feeding, through animal housing, till application to land (Chadwick et al., 2011).

Updated emission factors for N_2O (cumulative N_2O-N loss as a proportion of total N applied in the manure) for cattle manure application to agricultural land, have been pointed between 0.0031 and 0.0050 kg N_2O-N kg^{-1} TN in dry and wet climates, respectively (van der Weerden et al., 2021) and, in their recent synthesis, van der Weerden et al. (2023), pointed soil pH, soil clay content, soil water filled pore space (WFPS), rainfall and their interaction with animal type where excreta came from, between the drivers that significantly affect N_2O emission factors.

Nitrous oxide emissions from soil after manures application are caused by several microbial metabolic pathways as nitrification (Norton and Ouyang, 2019), denitrification (Pan et al., 2022) and many others (Butterbach-Bahl et al., 2013). When soil WFPS surpasses 60-65%, major N_2O emissions can be expected (Shakoor et al., 2021; van der Weerden et al., 2021).

Nitrous oxide emissions from slurries application to agricultural land are strongly influenced by management strategies like application timing, rate and method, impacting soil physico-chemical properties and microbiology (Chadwick et al., 2011). In their global meta-analysis, Zhou et al. (2017) reported an increase in N_2O emissions from manure and slurries application by 32.7% compared to chemical fertilizers: this was ascribed to the greater supply of labile C compounds acting as energy source for nitrifier and denitrifier microorganisms, and for microbial activity, leading to progressive O_2 depletion, increasing anoxic conditions and, in turn, promoting denitrification (Cayuela et al., 2017; Shakoor et al., 2021).

Appropriately, Chadwick et al. (2011) pointed that some legislation as the ‘Nitrate Directive’ (91/676/EEC) may result in a ‘win-win’ strategy, since while abating NO_3^- leaching losses, the reduction in indirect N_2O emissions comes as a consequence; while other regulations incentivizing the adoption of low trajectory techniques for slurries distribution, as open slot injection, to abate NH_3 volatilization may enhance soil conditions that favour N_2O production. In this regard, legislation should carefully indicate best slurries and manures application techniques that minimize these ‘pollution swapping’ risks.

1.2.2 Strategies to rise slurries-Nitrogen Use Efficiency

Nitrogen Use Efficiency (usually abbreviated as NUE) has been defined in a multitude of ways with many nuances (Cassman et al., 2002; Dobermann, 2005; López-Bellido and López-Bellido, 2001; Weih et al., 2018), however, it generally represents the rate of fertilizer-derived N that is taken up by cultivated plants over the whole N supply, and rising fertilizers-derived NUE maybe represents one of the oldest but always current challenges of Agronomy, as reflected by its pivotal role in FAO and UNs' Sustainable Development Goals agendas (Zhang et al., 2015).

Compared to chemical fertilizers, given their biological nature and intrinsically unstable constitution, manures and slurries require an even more accurate management once applied to crops as soil-improvers and fertilizers to achieve valuable NUE. Following the 4Rs Stewardship (http://www.ipni.net/4R), right fertilizer source at the right rate, at the right time and in the right place, is a prerequisite to achieve maximum NUE, while minimizing negative environmental externalities (Gu et al., 2023). Other agronomic and conservation practices, such as no-till farming and the use of cover crops, play a valuable role in supporting correct nutrients and fertilizers (including slurries) management (Thorup-Kristensen et al., 2003).

1.2.2.1 Application timing and rate

Synchronizing crop nutrients requirements with supplies is one of the objectives for Agronomy, and this is even more challenging with manures and slurries that strongly variate in composition (Marino et al., 2008). Timing and rate of application must consider a multitude of elements to sustain crop N requirements, while minimizing N losses. First, difference can be found between annual and seasonal crops in terms of N uptake potential: in fact, permanent grasslands can show longer N uptake periods compared to annual crops like maize (Abalos et al., 2016), and fertilization strategies with manures should adapt accordingly. However, each application timing comes with distinctive benefits and risks.

For instance, higher leaching losses can occur during rainy season (Ren et al., 2022); however, other variables can influence this common observation and, in fact, while Reinsch et al. (2018) reported higher losses in rainy autumn, others pointed early-spring application as more prone to undergo to NO_3^- leaching due to the absence of an actively N-uptaking crop (Stoddard et al., 2005; van Eerd and O'Reilly, 2009). Similarly, N_2O emissions were found to be higher after autumn (Kandel et al., 2018; Rochette et al., 2004; Wagner-Riddle et al., 2017) or late-spring (Hunt et al., 2019) application in grasslands, or without significant differences between these two moments (Abalos et al., 2016; He et al., 2018; Hernandez-Ramirez et al., 2009).

Similarly, for maize, while manures and slurry application at base dressing before seeding is a common practice in Italy as starter fertilizer, this is a crucial timing, since no culture that can actively uptake N is present at that time, and N losses may arise; thus, application techniques that minimize these N losses, as sudden incorporation to contrast NH_3 volatilization (Webb et al., 2010) should be adopted. Moreover, in-season N addition may rise crop NUE by improving synchronization between supplies and requirements (Cassman et al., 2002): for this reason, integrations with mineral fertilizers (Martínez et al., 2017) or further additions of slurries (Guido et al., 2020; Yin et al., 2019) at growing stages with high N requirements could be useful.

1.2.2.2 Application methods

Manures and slurries application methods deeply impact on N losses, with possible pollution swapping effects, where reductions in one N form are offset by increases in another (De Vries et al., 2015). Compared to surface broadcast, open slot application has been often reported as the most effective application technique to abate NH_3 volatilization from manures and slurries distribution (e.g., -62% in the emission factor [van der Weerden et al., 2021]) since volatilization increase with increasing residence time over soil surface (Sommer et al., 2006; Webb et al., 2010). Again, after injection, the exposure to environmental variables that usually promote NH_3 volatilization (e.g., wind speed and solar radiation) is reduced (Lovanh et al., 2010; Sommer and Hutchings, 2001).

However, as anticipated, side effects on N_2O emissions have been widely documented (Thorman et al., 2020; van der Weerden et al., 2021; Webb et al., 2010). This side effect has been mainly ascribed to creation of anaerobic microsites with increased availability of readily oxidizable C compounds and N from slurries that promote denitrification (Velthof and Mosquera, 2011). In this regard, Webb et al. (2010) suggested deep injection of slurries as a way to promote complete denitrification of N_2O to N_2 within the soil profile, before eventual emissions. However, other studies didn’t report this pollution swapping effect between NH_3 and N_2O (Bourdin et al., 2014; Sistani et al., 2010; Weslien et al., 1998), suggesting that site-specific climatic and edaphic properties may determine the overall effect of slurry application method on N losses.

Furthermore, the adoption of injection discs on grasslands has been questioned, due to the possible damage to the crop: Rodhe and Halling (2015) studied different types of injection discs with or without coulters to increase the room for slurry deposition. The authors found severe damages to grass sward at roots and crowns level with injectors followed by different types of tines, and higher potential for NH_3 losses with increase in the width of the slot. They also found higher damages to the crop with dry soil conditions and to rhizomatous than cespitose grass species. Again, cases of higher NO_3^- leaching after manures and slurries incorporation have been documented (Hansen et al., 2019), and may be affected by specific soil conditions that could negatively interact with subsurface application, such as shallow tile drains or shallow water tables (Dell et al., 2011).

Conventional Agriculture may supply N requirements with slurries and biological fertilizers in combination with chemical ones, with the first that can be distributed usually at pre-sowing, while the second for side-dressing (Federolf et al., 2016; Martínez et al., 2017); on the other hand, Organic Farming must rely solely on biological fertilizers (manures and crop residues): here the adoption of fertigation with slurries, can enhance N recovery efficiency by cash crops since N is supplied when their demand is maximal (Guido et al., 2020). However, while fertigating with slurries is not a novelty concept (Lowrance et al., 1998), there is still few research on this topic; and even less documented practical implementations, mainly due to practical constraints (see. 1.2).

1.2.2.3 Conservation practices: cover crops

Cover crops (CCs) are cultures grown between one main crop cycle and the following to attain several ecosystem services (Daryanto et al., 2018), like soil organic C enrichment (Ardenti et al., 2023; Koudahe et al., 2022), enhancing soil C cycling and biodiversity (Fiorini et al., 2022), weeds control (Daryanto et al., 2018; Tabaglio et al., 2008), soil protection from erosion (Blanco-Canqui et al., 2015) and exploitation of residual N from previous cash crops, thus reducing the risk of nitrate leaching towards groundwater (Blanco-Canqui, 2018; Thorup-Kristensen et al., 2003).

This final aspect is of uttermost importance: Brassicaceae and Poaceae have been identified between the most effective species families in reducing nitrate pollution of groundwaters, with 75% and 52% reduction respectively (Nouri et al., 2022). However, a wide range of 18% to 95% in the abatement of nitrate leaching has been reported (Blanco-Canqui, 2018), suggesting that many variables contribute to successful containment. Among others, the effectiveness has been shown to positively relate to the soil sand content (Nouri et al., 2022; Thapa et al., 2018), active uptake of nitrate by roots (Daryanto et al., 2018; Nouri et al., 2022), biomass production (Blanco-Canqui, 2018), and microbial immobilization induced by cover crops residue with high C/N ratio (Daryanto et al., 2018).

To maximize their agro-ecosystemic services, and within the principles of Conservation Agriculture (CA), cover crops' residue should be further retained in the field (Francaviglia et al., 2023): in fact, the mulching effect can prevent soil water from evaporating, reduce weeds infestation and sustain soil organic carbon storage, among others (Ranaivoson et al., 2017). Notwithstanding those positive effects, the role of cover crops' residue (and, in a broad sense, of all crops residues) on environmental externalities is contentious. For instance, some meta-analyses and reviews have investigated and deepened the role of CCs' residue on N_2O emissions: while in a critical global review, Abdalla et al. (2019) found no significant contribution of cover crops on direct N_2O emissions, Abalos et al. (2022a) identified crop immature residue as a potential source for N_2O emissions. Conversely, mature residue with high C/N ratio (> 30) can limit N availability for microorganisms that produce N_2O with immobilisation, but also for the following cash crop (Abalos et al., 2022a, 2022b; Boselli et al., 2020).

Besides those agro-ecosystemic services, the adoption of cover crops must not disregard the yield of the next cash crop. In their critical review, Abdalla et al. (2019) found an overall 4% decrease compared to no cover, but legume-non-legume mixtures increased yield by 13%. In their meta-analysis, Daryanto et al. (2018) found higher increase with legume cover crops (27%) than with non-leguminous (6%) and highlighted proportionally higher gains at zero N fertilization than with N addition. Accurate use of cover crops and organic fertilizers could guarantee the yields of the following cash crop, while maintaining the agro-ecosystem advantages deriving from the adoption of cover crops and the organic fraction of fertilizers. Milliron et al. (2019) observed an increase in silage maize production after late fall (November), compared to earlier, application of dairy slurry on a rye cover crop, with lower NH_3 losses and higher soil N content adopting injection, suggesting higher soil-N storage for following maize, however they reported some damages to rye from injection discs. Similar failures (-25% plant density) were also found by Singer et al. (2008) with a rye-oat cover crop. In this respect, Sherman et al. (2021) proposed several low disturbance manure application (LDMA) strategies, including sweep injection, strip till, band application and shallow disk injection.

In spite sometime after cover crops establishment, slurries and manures may also be applied concurrently with their seeding, and/or after their termination. While the former can be indicated to optimize utilization of manure-derived N by cover crops and reduce field work (Harrigan et al., 2006), the latter focuses on ready availability of nutrients for the following cash crop, so manures/slurries act as starter-fertilisers sustaining a rapid crop establishment (Battisti et al., 2023; Martínez et al., 2017). However, slurry application above (cover) crops residues may enhance NH_3 volatilization (Bless et al., 1991; Loyon and Guiziou, 2019), thus the technique should be carefully calibrated to minimize undesirable side-effects.

1.3 Objectives

The general objective of this thesis is to assess the potential of slurries (raw and treated) to sustain crops (permanent grasslands and maize) growth and N requirements, while minimizing adverse environmental impact of their adoption.

The specific objectives are:

i. To monitor N loss pathways (N_2O, NO_3^-, NH_3) after slurries - and synthetic fertilizers - application, to evaluate potential pollution swapping between the various forms, depending on the fertilization strategy.
ii. To evaluate different novel strategies to reduce N losses from manure distribution (subsurface injection and fertigation) and increase manure-derived NUE, in comparison with conventional manuring methods (surface distribution with splash plate).
iii. To assess the role of different agro-environmental scenarios on N losses after fertilization on crops. Grasslands, cover crops, conventional and organic maize cropping system are evaluated to develop targeted fertilization strategies to maximize NUE, while reducing negative environmental impacts.

Outline of this thesis

The following hypotheses resulted from the objectives of this thesis:

i. Slurry injection reduces NH_3 volatilization but with possible pollution swapping with N_2O emissions and NO_3^- leaching in different agro-environmental scenarios (permanent grassland and intensive maize).
ii. Cover crops residue may help in reducing N losses while sustaining maize yields.
iii. Fertigation with slurries is a feasible technique to sustain maize yields in organic agriculture while extending the fertilization period.

The thesis has 3 research chapters, next to a general introduction (Chapter 1) and a general discussion (Chapter 5).

In Chapter 2, we (i) monitored the main Nr loss pathways (i.e., NH_3 volatilization, N_2O emissions, and NO_3^- leaching) after liquid-separated cattle slurry application to a permanent grassland of the Po valley region; (ii) for this location, evaluated the best compromise between application method (i.e., surface broadcast and shallow injection) and timing (i.e., autumn, winter and spring) to gain better results in production and Nitrogen Use Efficiency (NUE), while minimizing Nr loss pathways.

In Chapter 3, we (i) investigated the mitigation potential of two widely adopted cover crops (i.e., rye [*Secale cereale* L.] and white mustard [*Sinapis alba* L.]) against main Nr loss pathways (i.e., NH_3,

N_2O and NO_3^-) both during their active growing stage and after their termination; (ii) evaluated the interaction between digested cattle slurry application method (i.e., surface broadcast *vs*. shallow injection) at maize pre-sowing and different type of cover crop residue on following maize NUE and on Nr loss pathways; (iii) separately studied the relative impact of these three different Nr loss pathways for “cover crops” (i.e., from cover crops seeding to their chemical termination), “digestate” (i.e., from pre-sowing application as starter fertilizer to urea application as side-dressing) and “urea” (i.e., from surface broadcast urea application as side-dressing to maize harvest) periods.

In Chapter 4, we (i) evaluated the feasibility of fertigation with liquid-separated and subsequently microfiltered cattle slurry for maize side-dressing under Organic Farming; (ii) tested three different strategies for maize fertilization with fertigation: whole N supply at pre-sowing with liquid-separated slurry (A); 50% N application at pre-sowing with slurry, followed by two interventions of fertigation at side-dressing to integrate the remaining 50% of N (A+P); whole N application through fertigation at side-dressing (P); (iii) monitored Nr loss pathways (i.e., NH_3 volatilization, N_2O emissions and NO_3^- leaching) through the maize cropping season.

Chapter 5 provides a general discussion on main results of the study and identifies future research needs.

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