High Nitrogen Availability but Limited Potential Carbon Storage in Anaerobic Digestates from Cover Crops

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High nitrogen availability but limited potential carbon storage in anaerobic digestates from cover crops

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Abstract

Cover crops are increasingly used for biogas production, a renewable energy source, without competing for food production. The behavior of the resulting digestates after soil application is poorly understood, which prevents their efficient recycling in agriculture and the environmental assessment of their application. The objective of this study was to quantify the nitrogen availability and potential carbon storage of cover crop-issued digestates after soil application. A total of 10 raw digestates, 2 liquid phases, and 3 solid phases after phase separation were sampled. Main cover crops used in the sampled biogas plants were winter barley, rye and maize. Classical physicochemical analyses and laboratory incubations to study their C and N mineralization were conducted. Despite a moderate C mineralization of raw and liquid digestates after 91 days, their initial limited carbon content induced, in the end, a low contribution to soil organic carbon (13 and 11 kg remaining C Mg^{-1} FM, respectively), similar to a pig slurry and much lower than a bovine manure. With a higher initial carbon content and lower C mineralization, the contribution of solid digestates to carbon storage could be higher if applied at a sufficient rate. Organic N mineralization of raw and liquid digestates was moderate, but their N availability was high (3 and 4 kg available N Mg^{-1} FM, respectively) thanks to their mineral nitrogen contents, similar again to a pig slurry. In contrast, that of solid digestate was almost null with a very low mineral N content and no organic N mineralization. Finally, all the digestates also brought significant amounts of P and K.

Keywords: digestate, cover crop, mineralization, carbon, nitrogen.

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1 Introduction

To increase renewable energy production the production of cover crops for anaerobic digestion is promoted in various countries (Marsac et al., 2019; Riau et al., 2021; Szerencsits et al., 2016). For example, the French agency for ecological transition published a prospective study about the complete substitution of fossil gas by renewable gas, which included the generalization of the use of cover crops for biogas production (with 50 10^6 Mg of dry matter harvested per year) (Ademe, 2018). In comparison to dedicated crops, the use of cover crops has the advantage to not compete with food production because harvested cover crops for biogas replace bare soil or non-harvested cover crops. Anaerobic digestion also results in the production of digestates that are used as organic fertilizers. Contrary to digestates from livestock effluents or dedicated crops, which are rather well known (e.g., Nkoa (2014), Möller & Müller (2012)), information on the digestates of cover crops is still rather scarce. To our knowledge, except for the chemical composition of two digestates reported by Marsac et al. (2019), there are no published results on the digestates of cover crops from real anaerobic plants. This lack of information prevents an adequate assessment of their agronomic and economic values in relation to the potential savings on mineral fertilizer. Moreover, the potential contributions of carbon digestate to soil organic matter (Cayuela et al., 2010) and of nitrogen digestate to the N supply to crops (Brockmann et al., 2018) are key factors to consider in the environmental assessment of organic waste recycling. These contributions are closely related to their C and N contents, but also to their C and N mineralization dynamics, which can be highly variable for different organic wastes (Lazicki et al., 2020; Levavasseur et al., 2021). Especially for digestates (excluding digestates of cover crops), the literature has reported both N immobilization (use of mineral N by microbial biomass during decomposition of organic matter) or net mineralization as well as low to high C mineralization (Cavalli et al., 2017; de la Fuente et al., 2013; Levavasseur et al., 2021). Specific results for digestates of cover crops are thus needed.

The objective of this study was to quantify the potential N availability and potential C storage related to the application of digestates made exclusively from cover crops and agro-industrial wastes, and with no animal manures as co-substrates. based on physico-chemical analyses of 15 digestates and laboratory incubations to study their C and N mineralization. The main hypothesis tested was whether cover crop-issued digestates had a high N availability and a limited C storage potential as other types of digestates.

2 Materials and methods

Digestates were sampled from 13 anaerobic digestion plants (wet mesophilic process) mainly located in Ile-de-France (Paris area, northern France). There were 10 raw digestates, 2 liquid, and 3 solid phases of digestate after phase separation (screw press). The 13 digesters differed in terms of feedstock (Online Resource, Table S1), with a proportion of cover crop (in % weight of fresh matter) ranging from 16% to 100% (mean proportion equal to 55%). Maize (*Zea mays L.*) was the main summer cover crop. It was typically sown immediately after the harvest of a winter crop (e.g., grain winter barley) in the end of June, ensiled in mid-October, and followed either by a winter cereal or a spring crop. Winter barley (*Hordeum vulgare L.*) and rye (*Secale cereal L.)* were the main winter cover crops. They were typically sown in the end of September or in the beginning of October, ensiled in the beginning of May, and followed by a spring crop

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(grain maize usually). The other digested wastes were mainly sugar beet pulp, cereal wastes, and food wastes. The hydraulic retention time (digester and postdigester) was usually greater than 100 days.

The raw digestates were sampled in the postdigester, while liquid and solid digestates were sampled just after phase separation. Samples were immediately frozen at -20°C to avoid any digestate evolution before analysis. The references for the analytical methods are in Table S2 (Online Resource). Dry matter, organic C, Kjeldahl N, N-NH_4, P, and K contents were analyzed (3 replicates, except for digesters 12 and 13) and compared to well-known organic fertilizers: pig slurry and bovine solid manure (mean characteristics retrieved from Houot et al. (2014)). In addition, soil and digestate mixtures were incubated for 91 days under controlled conditions (28°C, pF 2.5 corresponding to a soil water content of 0.17 g g^{-1}) to study the mineralization of organic C and organic N under standardized conditions (adapted from FD U44-163 and FD U42-163). Ninety-one days of incubation was estimated to represent one year in the field in the temperature conditions of central France (Levavasseur et al., 2021). The soil used for incubation was a decarbonated luvisol with a low carbon content (Online Resource, Table S3). Raw and liquid digestates were incubated fresh, whereas solid digestates were dried and ground before incubation. The application rate varied from 700 to 2000 mg C kg^{-1} dry soil. For solid digestates poor in mineral N, mineral N (KNO_3) was added in excess to reach at least a soil mineral N content of 35 mg N kg^{-1}. This avoided any mineral N deficiency, which could have limited the digestate decomposition rate, and highlighted the potential N immobilization (Recous et al., 1995). The CO_2 evolved, and the soil mineral N was measured to determine the mineralized C and N. The net C and N mineralized from each digestate were computed by subtracting the mineralized C and N of an unamended soil (control). The proportions of the net mineralized C and N from the digestates were obtained by dividing the net C and N mineralized from each digestate by the total amount of added organic C and organic N by the digestate, respectively. Additional information about the incubation experiment is given in Table S4 (Online Resource).

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The contributions to the soil organic matter of the digestate and to the N supply were computed as follows (the nitric N content of the digestate is neglected):

$$C_{remaining} = C_{org}\,(1 - C_{mine91}) \qquad (1)$$

$$N_{available} = N_{NH4} + N_{org}\,N_{mine91} \qquad (2)$$

where $C_{remaining}$ is the quantity of remaining C in the digestate (kg C Mg^{-1} fresh matter (FM)), C_{org} is the organic carbon content of the digestate (kg C Mg^{-1} FM), C_{mine91} is the proportion of mineralized organic carbon after 91 days of incubation, $N_{available}$ is the quantity of available N in the digestate (kg N Mg^{-1} FM), N_{NH4} is the ammoniacal N content of the digestate (kg N Mg^{-1} FM), N_{org} is the organic nitrogen content of the digestate (kg N Mg^{-1} FM) and N_{mine91} is the proportion of mineralized organic nitrogen after 91 days of incubation.

The indicator of residual organic carbon (I_{ROC}) proposed by Lashermes et al. (2009) was also determined from the biochemical fractions of the digestates (Van Soest and Wine, 1967) and the proportion of carbon in the digestate that was mineralized during a very short incubation (3 days). I_{ROC} has been defined as a predictor of C remaining from exogenous organic matter (EOM) after long-term incubation of EOM with soil under controlled conditions, and was shown to represent the C remaining in soils after years under field conditions (Levavasseur et al., 2020). Its original calibration was made on a database without digestates. The objective was thus to determine whether I_{ROC} was also a good predictor of residual digestate C at the end of the incubation.

To analyze the correlations between digestate characteristics and digester feedstocks, a correlation matrix was analyzed (R Development Core Team, 2013). Only raw digestates were used for this analysis because of the limited number of liquid and solid digestates in our dataset.

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3 Results and discussion

3.1 Chemical composition of digestates

The chemical composition of raw digestates, liquid digestates, and pig slurry were similar (**Fig. 1**, Table S5), with low dry matter (mean values of 61, 62 and 50 kg Mg^{-1} FM, respectively) and organic carbon content (21, 18 and 17 kg Mg^{-1} FM, respectively), moderate nitrogen content (4.7, 5.6 and 5.5 kg Mg^{-1} FM, respectively), and a similar to slightly higher proportion of nitrogen under mineral form for digestates (59, 65 and 55% total N, respectively). Solid digestates had similar characteristics to bovine manure. The variability of raw digestates was moderate, with coefficients of variation lower than 25% except for phosphorus. The contents of organic carbon and total phosphorus were positively correlated with dry matter content (Online Resource, Fig. S1).

The characteristics of our digestates were in the ranges reported in the review of Möller & Müller (2012) for various types of digestates. Our digestates were very similar to the digestate of silage maize reported by Wolf et al. (2014) for C and N contents. Despite different feedstocks, the present digestates were also very similar to the 20 digestates of various substrates studied by Risberg et al. (2017). For example, the raw digestates had a mean C content, total N content, and proportion of N under mineral form equal to 21 kg Mg^{-1} FM, 4.7 kg Mg^{-1} FM, and 59%, respectively, in comparison to 17 kg Mg^{-1} FM, 4.8 kg Mg^{-1} FM, and 71%, respectively, in Risberg et al. (2017) (recalculated).

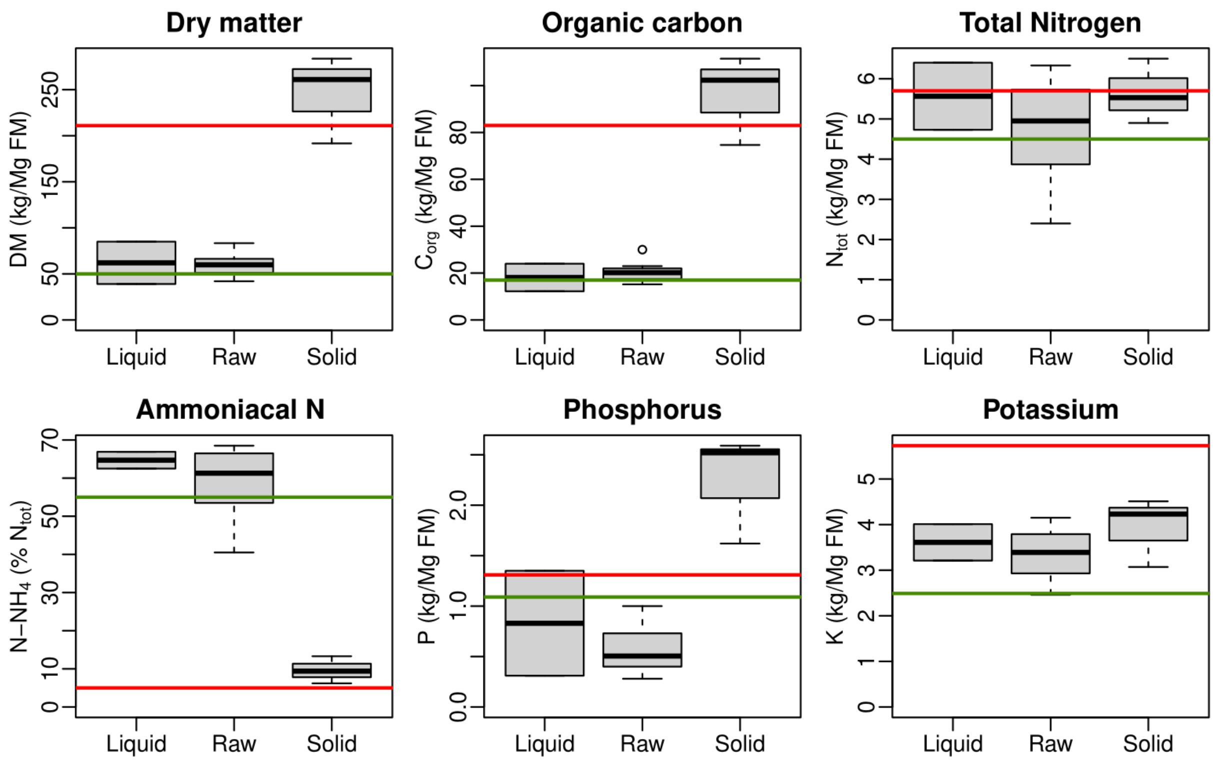

Fig. 1 Chemical composition of the studied digestates compared to a pig slurry (green line) and a solid bovine manure (red line). The digestate samples included 10 raw digestates, 2 liquid digestates and 3 solid digestates

3.2 Organic carbon and nitrogen mineralization

During incubation, we observed a first phase of rapid C mineralization for two to three weeks, followed by slower linear mineralization (**Fig. 2**), regardless of the digestate type. The mean proportion of C mineralized for raw digestates after 91 days was 360 mg C g^{-1} added C, and the variability was moderate (standard deviation equal to 109 mg C g^{-1} added C). The C mineralization of liquid digestates was similar (389 mg C g^{-1} added C on average), while that of solid digestate was lower (209 mg C g^{-1} added C on average). Focusing on raw digestates, the C mineralization after 91 days was strongly and negatively correlated with I_{ROC} (R=0.92, p value < 0.001, Fig. S1, Table S5 for I_{ROC} values), which confirmed the usefulness of this indicator to estimate the potential remaining digestate C in soil, although I_{ROC} was calibrated with a dataset of EOM without digestates (Lashermes et al., 2009). C mineralization was also positively but weakly correlated with the total nitrogen (R=0.76, p value < 0.05, Fig. S1, Online Resource).

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On average, the mineralization of organic N was low and linear for raw and liquid digestates (**Fig. 2**). In contrast, solid digestates exhibited a first phase of immobilization for approximately two weeks, followed by slow remineralization. The mineralization of organic N after 91 days was moderate for raw digestates (101 mg N g^{-1} added N) with a relatively high variability (standard deviation equal to 107 mg N g^{-1} added N); the mineralization after 91 days ranged from a net immobilization of -100 mg N g^{-1} added N to a net mineralization of 242 mg N g^{-1} added N. The net mineralization of organic N from liquid digestates was higher (207 mg N g^{-1} added N), but that of solid digestate was lower and negative (-25 mg N g^{-1} added N, still a net immobilization after 91 days despite remineralization). The N mineralization after 91 days for raw digestates was strongly and negatively correlated with total nitrogen content (R=-0.84, p value < 0.01, Fig. S1, Online Resource). Contrary to previous studies with various organic wastes (Lazicki et al., 2020; Levavasseur et al., 2021), N mineralization was not correlated with the $C:N_{org}$ ratio.

Raw and liquid digestates from cover crops exhibited a higher C mineralization and a lower N mineralization than the digestate of maize and rye silage (and 14% of chicken manure) reported by Reuland et al. (2022), with slightly different incubation conditions. Raw and liquid digestates from cover crops exhibited higher C and N mineralization than other types of digestates studied by Levavasseur et al. (2021), who found mean C and N mineralization of 274 mg C g^{-1} added C and -18 mg N g^{-1} added N, respectively. These latter values were similar for the solid digestates studied here. As already shown for other types of digestates (Cavalli et al., 2017; de la Fuente et al., 2013), phase separation leads to a solid phase of digestates with net N immobilization and lower C mineralization than raw or liquid digestates.

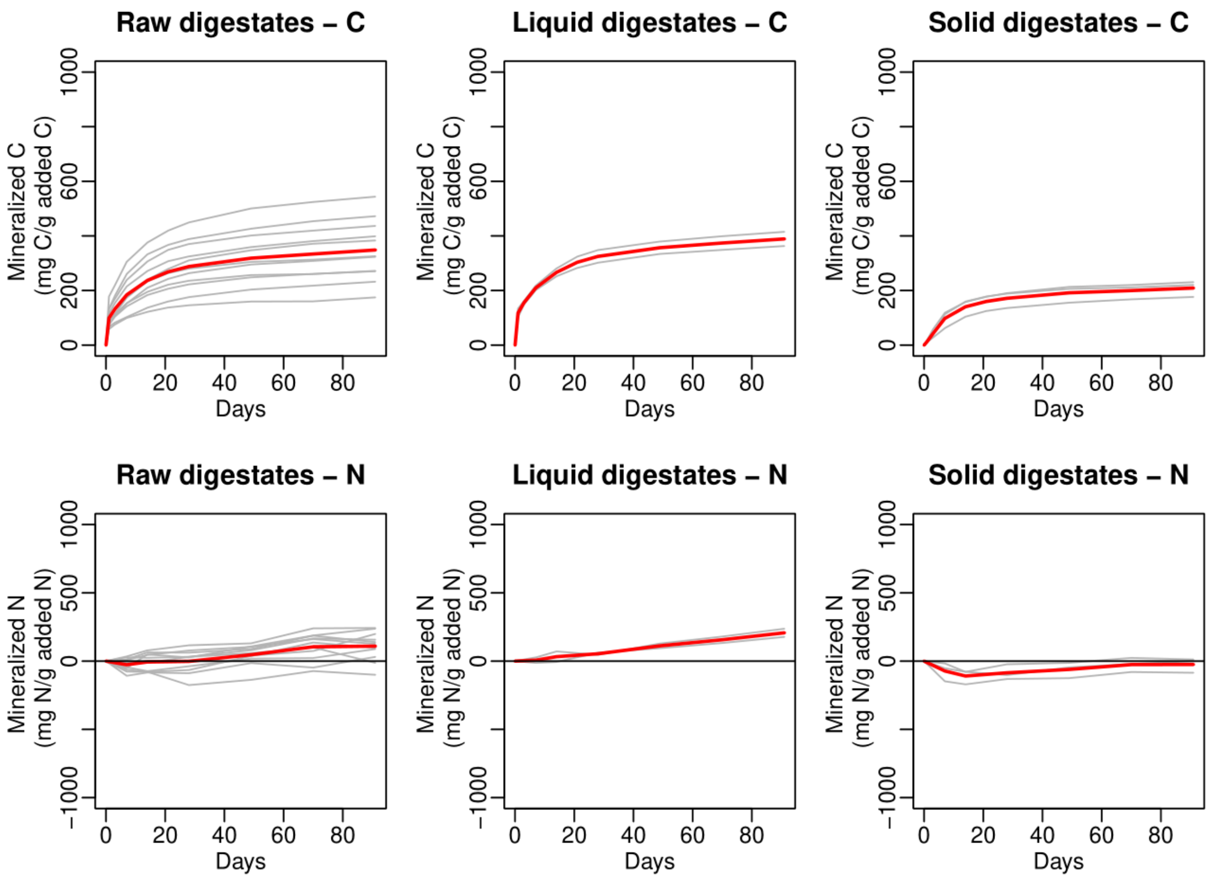

Fig. 2 Observed mineralized organic carbon and nitrogen for the raw (n=10), liquid (n=2), and solid (n=3) digestates during laboratory incubations. Each gray line represents a digestate incubation, while the red lines represent the mean mineralization for all digestates

3.3 Effect of digester feedstock on digestate characteristics

The proportion of cover crops in the digester feedstock was significantly and negatively correlated with total nitrogen content (R=-0.81, p value < 0.01, Fig. S1, Online Resource). This effect was weak and mainly induced by the digestate from cover crops only. These results are in line with Risberg et al. (2017) who found a limited effect of digester feedstock on digestate characteristics, but in contradiction to Guilayn et al. (2019), who found the opposite. Our study contains, however, fewer samples than that of Guilayn et al. (2019) and less diverse feedstock.

The proportion of cover crops in the digester feedstock was significantly and negatively correlated with C mineralization (R=-0.73, p value < 0.05, Fig. S1, Online Resource), but not with N mineralization. Among the other feedstocks, only the proportion of food waste in the digester was significantly and positively correlated with the proportion of C mineralized

(R=0.72, p value < 0.05, Fig. S1, Online Resource). However, these latter substrates concerned only two digesters.

3.4 Nutrients supply and potential C storage at usual rates

Considering the usual rates of application for raw, liquid, and solid digestates, which were 40, 40, and 10 Mg ha^{-1}, respectively (according to a survey of the farmers associated with the digesters), the quantity of nutrients applied to the field was computed, with the mean digestate characteristics presented in section 3.1 (Table 1). At these rates, raw and liquid digestates brought a large amount of available N (mainly N-NH_4) and phosphorus, similar to the amount of mineral N and P applied yearly in northern France (Moinard et al., 2021), while K was in excess. In contrast, the total C and remaining C applied were rather low in comparison to the application of solid bovine manure at a usual rate of 30 Mg ha^{-1}. They may, however, contribute to SOC storage in the case of repeated applications, as suggested by Tambone et al. (2019). The application of solid digestate provided a limited amount of nutrients, mainly P and K, and a limited amount of total C and remaining C. In addition to the difference in the quantity applied, the comparison of raw, liquid, and solid digestates must be made cautiously; these digestates come from different digesters with different feedstocks and processes that may impact the digestate characteristics (Bareha et al., 2021).

Finally, the nitrogen of digestate available to plants will depend on pedoclimatic conditions and their insertion in cropping systems. For example, the available N mainly relies on ammoniacal N; thus the limitation of ammonia volatilization will be a key issue, as already highlighted by many authors on digestates (Riva et al., 2016). Concerning phosphorus, its availability depends on the feedstock of the biogas plant, on the considered phase (liquid/solid) and on soil pH, but can be high (Tuszynska et al., 2021).

Table 1 Mean input with the studied digestates (10 raw digestates, 2 liquid phases, and 3 solid phases) applied at usual rates in comparison with typical organic fertilizers

Parameter	Raw digestate	Liquid digestate	Solid digestate	Pig slurry	Bovine manure
Fresh matter (Mg ha^{-1})	40	40	10	40	30
Dry matter (Mg ha^{-1})	2.4	2.5	2.5	2.0	6.3
Organic C (kg ha^{-1})	821	725	962	680	2490

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Remaining C (after one year in the field)[a] (kg ha^{-1})	519	437	762	373	1743
Total N (kg ha^{-1})	189	223	56	180	171
N-NH_4 (kg ha^{-1})	107	141	3	99	9
Available N (after one year in the field) (kg ha^{-1})	114	157	2	115	14
P (kg ha^{-1})	23	33	22	44	39
K (kg ha^{-1})	134	144	39	100	172

[a] The remaining C was computed as remaining C after 91 days of incubation

4 Conclusion

Raw and liquid digestates from cover crops appeared as potential efficient N fertilizers, similar to pig slurry, mainly due to their high content of mineral N. Applied at usual rates (40 Mg ha^{-1}), they could bring a significant portion of the N, P, and K required by an intensive cereal crop rotation in central France. On the other hand, their contribution to soil organic carbon is limited but could be significant with repeated applications. In contrast, the direct N availability of solid digestate was very limited, while its contribution to soil organic carbon could be higher if applied at a large enough rate. It could also possibly be a valuable substitution for mineral P fertilizer. This better knowledge of such rather new digestates from cover crops could be used to better manage their use by farmers and allow for an environmental assessment of their recycling in agriculture with the help of soil-crop models calibrated with these data.

Statements and Declarations

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Vincent Jean-Baptiste is employed by GRDF.

Financial and non financial interests

The authors have no relevant financial or non-financial interests to disclose.

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