

Application of Mineral Concentrates from Processed Manure

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5.5

Application of Mineral Concentrates from Processed Manure

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5.5.1 Introduction

Manure is a valuable source of nutrients for crops. However, in regions with intensive livestock farming systems and limited agricultural land, the amount of nutrients available exceeds the nutrient demand of crops. In these regions, the surplus of nitrogen (N) and phosphorus (P) results in an increase in soil nutrient status and high emissions of N and P to groundwater, surface water, and the atmosphere [1]. A series of policies and measures have been implemented in the European Union (EU) to decrease emissions of N and P from agriculture to the environment [2]. Processing of manure is considered as an option to increase the nutrient use efficiency of manure [3]. One treatment method is separation of livestock slurry into a solid fraction (SF) and a liquid fraction (LF) followed by reverse osmosis (RO) of the LF [4, 5]. The RO decreases the volume of the LF (Chapter 4.3), resulting in a concentrated N–potassium (K) solution ("mineral concentrate"), in which most of the N is present as ammonium (NH_4^+). The SF is rich in organic matter (OM) and P, and can be used as a soil amendment. The water removed by RO has low concentrations of nutrients

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and can be discharged to sewer or surface water [6]. The reduction of the volume by RO increases the ability to transport mineral concentrates from areas with high livestock density to arable farming areas. This chapter presents an overview of the nitrogen fertilizer replacement value (NFRV) of mineral concentrates from processed manure, based on a series of studies carried out in the Netherlands. In Section 5.5.2, an assessment is made of the fertilizer value of manure concentrates on the basis of the composition. Section 5.5.3 presents N fertilizer values obtained in pot and field experiments. Section 5.5.4 deals with N losses from mineral concentrates as ammonia (NH_3), nitrous oxide (N_2O), and nitrate (NO_3^-).

5.5.2 Product Characterization

Table 4.3.1 shows the average composition of mineral concentrates obtained from slurry treatment based on separation and RO. The average total N content of the concentrates is 8.15 g N kg^{-1} product. The N in mineral concentrates is mainly found in the NH₄⁺ form (on average, 90% of total N in the concentrate). The remaining N is organically bound. The pH of mineral concentrates is high (about pH 8), thus it is likely that NH₄⁺ partly occurs in the form of NH₃ in mineral concentrates.

The efficiency of N in mineral concentrates as a fertilizer depends on the presence and degradability of organic N and the gaseous N losses (as NH_3 and via denitrification) during and after application [7]. The NFRV of an organic fertilizer is the percentage of the applied N that has the same effect on crop N yield as mineral N fertilizer. In the Netherlands, NFRV is generally determined by comparison with broadcast mineral fertilizer calcium ammonium nitrate (CAN), which is the most commonly used mineral N fertilizer in the country.

Part of the N in mineral concentrates becomes available for the crop via N mineralization. According to fertilizer recommendations in the Netherlands (www.bemestingsadvies .nl; www.kennisakker.nl), it is assumed that the NFRV of organic N in manure amounts to 20–60% during the first 12 months after application. The NH₃ emission from surface-applied slurry amounts to 69–74% of applied NH_4^+ -N and that from slurry injected in the soil (including injection) is 2–26% [8]. Assuming that these figures also hold for mineral concentrates, it is estimated that the NFRV of surface-applied mineral concentrates is 25–30% and that of injected slurry 70–90% compared to CAN. This theoretical approximation of NFRV has been tested in experiments, the results of which are presented in Section 5.5.3.

The P content in mineral concentrates is generally low ($<0.2 \text{ g P kg}^{-1}$; Chapter 4.3), and therefore mineral concentrates have no agronomic value as P fertilizers.

The K content in mineral concentrates is about 8 g K kg⁻¹ (Chapter 4.3). The exact chemical form in which it occurs in mineral concentrates is not known, but based on chemical analysis it is assumed that it is found bound to bicarbonate, chloride, and sulfate and in fatty acids [9]. Therefore, it is likely that the K in mineral concentrates is fully available to the crop. The supply of K in mineral concentrate reduces the need for other mineral K fertilizers. This is particularly advantageous for crops with a high K demand such as potato and maize. The K demand of grassland is also high, but is partly met when cattle manure is produced on a farm. An excess supply of K to cattle can cause health problems (grass tetany). The amounts of K in feed, fertilizer, and manure should hence be taken into consideration when importing mineral concentrates to a dairy farm. Mineral concentrates also contain other nutrients, including calcium (Ca), magnesium (Mg), sulfur (S), sodium (Na), and trace elements. If a concentrate is applied at common N and K application rates, the supply of most other nutrients is not of agronomic importance. However, the levels of Na in mineral concentrates are approximately 20–25% (w/w) that of K [9]. When using a mineral concentrate as an N or K fertilizer, a significant amount of Na is applied (20–40 kg Na ha⁻¹). Na has value in animal feeding, and some arable crops (e.g. sugar beet) respond positively to its application. S is also a valuable component of mineral concentrate, but the average total S application rate is low (about 4 kg per 100 kg N as mineral concentrates is unknown. The average CL concentration is 3 g kg⁻¹ mineral concentrates, as long as the supply of Cl with other fertilizers is taken into account.

The contents of the heavy metals Cd, Cr, Ni, Pb, and As and of organic contaminants such as dioxins, non-ortho PCBs, mono-ortho PCBs, indicator PCBs, organochlorine pesticides residues, polyaromatic hydrocarbons (PAHs), and mineral oil in mineral concentrates are low, and often below the detection limit. These contents meet the standards in the Fertilizer Act of the Netherlands [10]. Consequently, it is unlikely that the use of a mineral concentrate as fertilizer will lead to an unacceptable loading of soil with heavy metals and organic contaminants.

5.5.3 Agronomic Response

5.5.3.1 Pot Experiments

Pot experiments to test the NFRV of mineral concentrates, using grass as a test crop and CAN as a reference fertilizer, have been carried out by Ehlert et al. [11], Klop et al. [12], and Rietra and Velthof [13]. CAN consists of 27% N, of which half is nitrate and half is ammonium. In these pot experiments, the NFRV of injected mineral concentrate compared to broadcast CAN was on average 91%, and higher than that of injected pig slurry (75%; Table 5.5.1). These findings are in agreement with the theoretical NFRV estimated from the chemical composition (Section 5.5.2).

In Klop et al.'s experiment [12], grass yields of surface-applied mineral concentrate were low, partly due to scorching of the grass after surface application of the mineral concentrate.

References	Crop	NFRV, % of CAN				
		Mineral concentrate		Pig slurry		
		Injected	Surface-applied	Injected	Surface-applied	
[12]	Grass	96	50	79	41	
[11]	Grass	86	_	74	_	
[11]	Swiss chard	87	_	71	_	
[13]	Grass	93	72	76	_	
Average		91	—	75	—	

Table 5.5.1 Average nitrogen fertilizer replacement value (NFRV) of injected mineral concentrate and injected pig slurry compared to calcium ammonium nitrate (CAN) (in %) in pot experiments.

The same held with surface-applied pig slurry. Scorching did not occur after injection of mineral concentrate or pig slurry or after surface-application of CAN. Deposition of urine during grazing has also been shown to induce scorching of grass [14]. Probably, salt, NH₃, and volatile fatty acids concentrations near the grass roots were too high after surface application of mineral concentrate and pig slurry but not after injection. Part of the difference between surface application and injection is due to differences in NH₃ emissions. The NFRV of pig slurry was only 41% after surface application, and increased to 79% when injected [12]. Measurements showed that NH₃ emission was much lower from injected concentrate than from surface-applied concentrate. Emission of N₂O from mineral concentrate was higher than from CAN, but lower than from pig slurry.

In Ehlert et al.'s experiment [11], the NFRV of mineral concentrate was tested with perennial rye grass and Swiss chard and with different types of mineral N fertilizer. The NFRV of mineral concentrate compared to CAN was on average 87%. The NFRV of liquid ammonium nitrate (AN), ammonium sulfate (AS), and ammonium chloride was on average 100% compared to CAN. This indicates that the efficiency of solid ammonium fertilizers was higher than that of mineral concentrate in this experiment. The NFRV of urea was somewhat lower (except when applied to grass on a sandy soil), probably due to NH₃ emission [15].

In Rietra and Velthof's experiment [13], the effects of soil moisture content and acidification of mineral concentrate on NFRV were tested. Acidification is a measure to decrease NH₃ emission [16]. The NFRV of injected concentrates (84–93%, with the highest NFRV at the highest moisture content) was significantly higher than that of surface-applied concentrate (64–79%). The NFRV of acidified concentrate was similar to that of CAN. Measurements showed that acidification minimized NH₃ emission.

5.5.3.2 Field Experiments

Field experiments in the Netherlands show NFRVs of injected (to a depth of 5 cm) mineral concentrates ranging from 54 to 84% compared to broadcast CAN (Table 5.5.2). The lowest NFRV, 54%, was observed on grassland in 2009. An explanation for this relative outlier is as yet lacking. Averaged over all experiments, the NFRV of mineral concentrate compared to CAN was 79% on arable land and 71% on grassland. These values are lower than those obtained in the pot experiments (Table 5.5.2) and at the lower end of the theoretically estimated NFRV values of 70–90% (Section 5.5.2). Van Geel et al. [21] also determined the NFRV in field experiments, with a less detailed set-up than the experiments described in Table 5.5.2. Their results showed a wide range in NFRV (0–130%). In 20 experiments, the NFRV of mineral concentrate was similar to CAN, in 10 it was lower than CAN, and in 1 it was higher than CAN [21].

The NFRV of mineral concentrates was higher (79–117%, average 93%) when compared to liquid ammonium nitrate injected with the same equipment as mineral concentrate. Clearly, the application method and form of fertilizer affect N use efficiency; that is, the N use efficiency of an injected liquid N fertilizer (liquid ammonium nitrate and mineral concentrate) was lower than that of broadcast CAN prills. The distribution of N in the soil differed between broadcast-applied CAN and injected liquid fertilizers, and this could be a factor in the differences in N use efficiency between CAN and the liquid fertilizers.

Crop	Year	Soil type	NFRV, %		References
			Compared to CAN	Compared to liquid AN	
Potato	2009	Clay	76		[17]
Potato	2009	Sand	84		[17]
Potato	2010	Clay	75	117	[17, 18]
Potato	2010	Sand	81		[17]
Maize	2010	Sand	72		[19]
Maize	2011	Sand	84		[19]
Grassland	2009	Sand/clay	54 ^a	86	[20]
Grassland	2010	Sand/clay	71 ^a	102	[20]
Grassland	2011	Sand	80 ^a	79	[20]
Grassland	2012	Sand	81 ^a	83	[20]

Table 5.5.2 Average nitrogen fertilizer replacement value (NFRV) of injected mineral concentrate compared to calcium ammonium nitrate (CAN) or liquid ammonium nitrate (AN) (in %) in field experiments.

^a For each year, the average NFRV of two to four experiments is included.

The results of the experiments indicate that there is scope to increase NFRV in the field by optimizing the use of mineral concentrate via low NH₃ emission application techniques and by decreasing the organic N content of mineral concentrate.

5.5.4 Risk of Nitrogen Losses

5.5.4.1 Ammonia Emission

Mineral concentrate is an NH_4^+ -containing fertilizer with a high pH (about 8), and therefore it carries a risk of NH_3 emission. Injection into the soil is a well-known NH_3 emission abatement technique [22]. A review by Hou et al. [23] showed that emissions of NH_3 from slurries following band spreading, incorporation, and injection were 55% (range: 37–67%), 70% (50–82%), and 80% (72–86%) lower than those from surface applied manures, respectively.

In a series of incubation studies, the NH₃ emissions from untreated pig slurry, mineral concentrate, mineral fertilizers, and the SF of separated slurry were quantified [24]. The products were both surface-applied and injected in the soil at 5 cm depth. Surface application of mineral concentrate, pig slurry, and urea resulted in high NH₃ emissions (Figure 5.5.1). The NH₃ emission from injected mineral concentrate was low, similar to that of surface-applied CAN (Figure 5.5.1). Averaged over three incubation tests, the NH₃ emission from injected mineral concentrate was significantly lower than that of injected pig slurry [24].

In a review, Hou et al. [23] found significantly lower NH_3 emissions (reduction with 18% based on 44 observations) for separated LF relative to untreated slurry. The NH_3 emissions from mineral concentrates and LF were not determined in the same experiment, so it is not clear if NH_3 emission from mineral concentrates differs from that from LF under the same conditions. Differences in NH_3 emission may be expected because of the higher NH_4^+ concentration of mineral concentrates compared to the LF or the lower water content of



Figure 5.5.1 NH₃ emissions from calcium ammonium nitrate (CAN), urea, urean (liquid mixture of urea and ammonium nitrate), pig slurry, mineral concentrate, and the SF of separated slurry applied at equal amounts of total N. All fertilizers and manures were both surface-applied and injected (indicated as incorporated). Source: Results of an incubation experiment with arable sandy soil by Velthof and Hummelink [24].

mineral concentrates, as a result of which the infiltration rate into the soil may be reduced. Because of these differences, the NH_4^+ concentration gradient at the liquid–air interface will be greater after application of mineral concentrate than after application of LF.

Field experiments in 2010 showed that the NH_3 emission after sod injection in cereals was 3% of the applied NH_4^+ -N in the mineral concentrate, or 12% when applied via trailing hoses [25]. The NH_3 emission from mineral concentrate applied to grassland via sod injection averaged 8% of the applied NH_4^+ -N. These measurements were carried out in just one year, and thus the emission factors cannot be generally applied, as weather conditions have a major effect on NH_3 emission [26].

The risk of NH_3 emission from applied mineral concentrate is probably higher when applied to soils containing lime than to neutral or acidic soils, as is the case for any other NH_4^+ -based mineral fertilizer [15]. Additional NH_3 abatement techniques may be applied to decrease NH_3 emission and increase N efficiency. Rietra and Velthof [13] showed in a pot experiment that acidification of mineral concentrates minimized NH_3 emission. The NFRV of acidified mineral concentrate was equal to that of CAN.

5.5.4.2 Nitrous Oxide Emission

In a series of incubation studies, Velthof and Hummelink [24] quantified N_2O emissions from untreated pig slurry, mineral concentrate, and mineral fertilizers (see Figure 5.5.2 for the results of the experiment with grassland soils). The average N_2O emission of injected mineral concentrate was higher than the N_2O emission from a similar N rate of



Figure 5.5.2 N_2O emission factors as per cent of N applied for calcium ammonium nitrate (CAN), urea, urean, pig slurry, and mineral concentrate (MC) applied to intact grassland columns (PVC columns with a diameter of 10 cm and height of 10 cm) from clay, sand, and peat soils. The application rate was equivalent to 170 kg N ha^{-1} . CAN, urea, and urean were surface-applied and the pig slurry and mineral concentrates were injected in a row at 5 cm depth with a knife. The soil moisture content was kept at field capacity and incubation was carried out at 20°C. Source: Results of a 14-day experiment under controlled conditions by Velthof and Hummelink [24].

surface-applied CAN [24]. The N_2O emission from mineral concentrate was approximately 1.5-fold higher than that from untreated pig slurry, averaged over all studies and application techniques [24]. The injection of mineral concentrate and pig slurry resulted in higher N_2O emissions than surface application.

Both nitrification and denitrification may be sources of N_2O after application of mineral concentrates to a soil. Application of mineral concentrates may strongly increase concentrations of NH_3 in the soil. Ammonia is toxic for nitrifying organisms. A high NH_3 concentration in soil may thus inhibit nitrification, leading to the production of nitrite and N_2O [27, 28]. These effects are likely to be similar to those found in urine patches [29] and after application of anhydrous ammonia as fertilizer [30]. As for denitrification-related N_2O production, it must be noted that mineral concentrates contain organic carbon, including volatile fatty acids [11]. When degradable OM is applied to a nitrate containing soil under wet conditions, denitrifying bacteria may use the carbon as an energy source, and nitrate can be transformed into gaseous N_2O and N_2 . Paul and Beauchamp [31] showed that volatile fatty acids are effective energy sources for denitrifiers. Accordingly, Ehlert et al. [11] found that application of mineral concentrates to soil increased potential denitrification. The higher N_2O emission from injected mineral concentrate compared with surface-applied mineral concentrate is probably related to the lower oxygen concentrations in the soil, and the higher N concentrations after injection [32].



Figure 5.5.3 Average NO_3^{-} -N concentration (mg NO_3^{-} -N per I^{-1}) in the upper groundwater in a field experiment with maize on sandy soil carried out in 2010 and 2011. Calcium ammonium nitrate (CAN), mineral concentrate, pig slurry, and the solid fraction (SF) of separated pig slurry were applied at 150 kg N ha⁻¹. The experiment was carried out with and without a rye winter crop [19].

The amount of N lost via N_2O emission is low (usually less than 2% of the N applied as fertilizer or manure; [33]). Similar amounts will be lost in the form of NO_x [34]. Emissions of N_2 can be much higher than those of N_2O , especially under wet conditions [35]. The total gaseous N losses as N_2O , NO_X , and N_2 by nitrification and denitrification may significantly affect the N efficiency of mineral concentrates.

5.5.4.3 Nitrate Leaching

Mineral N in the soil in the fall is an indicator for the risk of NO_3^- leaching in winter in the Netherlands [36]. Measurements of mineral N contents in the soil after harvest in fall showed overall no differences between CAN and mineral concentrates in experiments with potato, maize, and grassland [17–20]. These results suggest that the use of mineral concentrate does not increase the risk of NO_3^- leaching compared to CAN.

Measurements in 2010 and 2011 of the NO_3^- concentration in the groundwater of the field experiments with maize showed that it was on average lower in the plots to which mineral concentrate was applied than in those that received CAN and pig slurry (Figure 5.5.3). A winter cover crop significantly reduced leaching of NO_3^- . In these maize experiments, the NFRV of mineral concentrate was 72–84% that of CAN. The lower NFRV did not increase N leaching losses from concentrates compared to CAN, however. Immobilization of mineral N probably didn't occur either [11]. A reduced availability of N from mineral concentrate due to an incomplete mineralization is also not likely, given the low content (5–10%) of organic N in mineral concentrates. These results indicate that the lower NFRV of mineral concentrates compared to CAN in these experiments was most likely related to gaseous N losses by denitrification and NH₃ emission.

Measurements of NO₃⁻ concentrations in the upper groundwater in a grassland experiment in 2012 showed no clear differences in nitrate concentration between mineral concentrate and CAN [20]. In an experiment by Schils et al. [37], NO₃⁻ concentration in upper groundwater was measured in 10 maize and 20 grassland farm fields. In one part of each field, mineral fertilizer and cattle slurry were applied, while in another part, mineral fertilizer was replaced by mineral concentrate at a comparable total N rate. The variation in NO₃⁻ concentration was large, and concentrations were higher in maize land than in grassland. There was no statistically significant difference in NO₃⁻ concentration between the two nutrient-management treatments.

These studies show that the risk of NO_3^{-1} leaching from applied mineral concentrates is similar to or lower than that with CAN, for both grassland and arable land. The N leaching losses from slurries were higher than those from mineral concentrate, probably due to release of mineral N by mineralization outside the growing period of the crop. The organic N contents of mineral concentrates were much lower than those of untreated slurries.

5.5.5 Conclusion

Mineral concentrates are N-K fertilizers produced by RO of the LF of separated livestock slurry. About 90% of the N in mineral concentrate is present as ammonium, the other 10% as organic N. Pot experiments showed that the NFRV of injected mineral concentrate was on average 91% that of CAN, and higher than that of injected pig slurry (75%). In field experiments in the Netherlands, NFRVs of injected mineral concentrates ranged from 54 to 84% compared to broadcast CAN. Injection of mineral concentrate into the soil strongly decreased NH₃ emission in incubation experiments, but increased N₂O emission. Field measurements show that the risk of nitrate leaching from applied mineral concentrates is similar to or lower than that from CAN and untreated manure. Obviously, NH₃ emission and denitrification are the dominant N-loss pathways after application of mineral concentrate. Losses of N after such applications can be decreased and NFRV can be increased by using low-NH₃-emission application techniques, acidification, and a reduction of the organic N content of the concentrate.

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