AGRICULTURAL AND FOOD SCIENCE

Agricultural and Food Science (2024) 33: xx–xx

https://doi.org/10.23986/afsci.142012

Pulp mill sludges as a solution for reducing the risk of mineral nitrogen leaching from agriculture

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Nitrogen (N) from agricultural systems contributes to the eutrophication of waterbodies through leaching. Incorporating organic material with a high carbon-to-nitrogen (C/N) ratio, such as mixed pulp mill sludges (PMSs), into the soil in autumn could reduce the amount of leachable N. This study tested the potential of composted and lime-stabilised mixed PMSs (CPMS and LPMS) in reducing the concentration of mineral N in the soil, and thus the risk of N leaching from arable land in the boreal region using a two-year field experiment. To better understand the mechanisms of the PMSs for influencing mineral N concentration in soil, the impact of PMSs with different quality on the reactions of N in the soil was investigated in a laboratory incubation study. In the field experiment, nitrate-N (NO_3^--N) concentration was lower with PMSs compared to mineral fertilisation and the control during the first autumn and the following spring after PMS application. The undersowing of Italian ryegrass reduced the NO_3^--N concentration in the soil during the first autumn. In the incubation experiment, PMSs reduced the soil ammonium-N (NH_4^+-N) concentration at the beginning of the experiment and the soil NO_3^--N concentration throughout the experiment compared to a mineral fertiliser treatment and an organic fertiliser. Increased soil respiration in PMS-treated soils indicated increase in microbial activity, and thus immobilisation of soil NO_3^--N and NH_4^+-N due to PMSs addition. These results suggest that PMSs have the potential to reduce N leaching from agricultural soils. However, the immobilisation of N must be considered when planning the nutrient requirements of the following crops.

Key words: primary sludge, secondary sludge, soil amendment, recycled fertiliser, nutrient recycling, nitrogen leaching

Introduction

Nitrogen (N) leaching from agricultural systems contributes to the eutrophication of waterbodies and possibly to the reduction of soil fertility. The global N flux through rivers has increased by approximately 78% in the past 150 years due to the introduction of industrial fertilisers and the increased cultivation of N-fixing legumes. The global N flux is expected to reach 62 Tg N a^{-1} by 2050 (Galloway et al. 2004). Finnish agriculture is a source of ca. 45 000 Mg N a^{-1} entering watercourses (38% of total N export to watercourses in Finland), approximately two-thirds of which end up in the estuaries of the Baltic Sea (Lepistö et al. 2006). Excess available inorganic N in water promotes algal growth due to the high rate of nutrient utilisation by algae (Ryther and Dunstan 1971). In Finland, many lakes and marine areas are seriously affected by eutrophication, and coastal waters, in particular, are highly eutrophic (SYKE 2024). Of the various N-containing compounds, NO_3^--N is the most susceptible to leaching, as it cannot be adsorbed onto soil particle surfaces (Jaakkola 1984). A key to minimising N export from fields is to reduce the amount of leachable N in the soil when the risk of leaching is greatest. Annual precipitation, currently 500–600 mm in southern Finland (FMI 2023), is predicted to increase in the future due to climate change (Ruosteenoja et al. 2016). Most of this precipitation falls in late summer and in autumn just before and after harvest of spring-sown crops. Heavy rainfall between August and November leads to increased water movement through the soil profile and increases the risk of N leaching, especially if the soil remains bare after harvest and the soil temperature is high, which promotes N mineralisation. Furthermore, the changing climate will likely lead to milder winters and an increase in winter precipitation (Peltonen-Sainio et al. 2009). At present, soil temperatures stay below 5 °C from November to April in Southern Finland (Yli-Halla and Mokma 1998, FMI 2021), which limits N mineralisation and immobilisation. In the future, rising temperatures will lengthen the period with favourable conditions for microbial activity.

Received 14 December 2023 / Accepted 6 April 2024
The Scientific Agricultural Society of Finland

The means of reducing N leaching include using various cover crops, including small-grain cereals, grasses, legumes and crucifers (Thorup-Kristensen 2001, Känkänen and Eriksson 2007, Kaspar et al. 2012, Tuulos et al. 2015). For example, Lemola et al. (2000) observed a reduction in soil NO_3^--N leaching (53% in clay soils, 63% in sandy soils) with Italian ryegrass as a catch crop under boreal conditions. Valkama et al. (2015) found that Italian ryegrass depleted the soil N concentration by an average of 60% in clay and coarse-textured mineral soils, which was the highest depletion rate among the undersown catch crops studied. One alternative for reducing N leaching is to use organic soil amendments with a high carbon to nitrogen (C/N) ratio (i.e., with high microbial available energy and low N content) before the season with the high leaching risk. Microbes use N for amino acid synthesis, and a net immobilisation of available N occurs in the soil if the microbially decomposed organic matter has a low N content. In general, organic matter with a C/N ratio above 25 results in a net immobilisation of N in the soil (Paul 2007), as such organic matter does not provide enough N for the microbes. Prolonged immobilisation of N in the soil during autumn and winter should reduce N leaching. However, the addition of organic material with a high C/N ratio to the soil and the following immobilisation of N may affect availability of N for the plants, and thus the yield of the following crop.

Pulp mill sludges (PMSs), i.e., solid wastes and by-products of the forest industry are one type of organic amendment. PMSs, especially primary PMSs, have a relatively high C/N ratio. Pulp and paper mills generate a large amount of waste, estimated at ca. 100 t for every 550 t of pulp produced (Haile et al. 2021). In Finland, the pulp and paper industry produces 578 000 t (dry matter, DM) of sludges annually (Marttinen et al. 2017). These sludges are derived from two sources: primary sludge from primary clarification and biological or secondary sludge from biological treatment (Monte et al. 2009). Primary sludges have a high C/N ratio and consist mainly of wood fibres (Vance 2000) with 15–35% hemicellulose, 40–45% cellulose and 20–30% lignin (Camberato et al. 2006). Secondary sludges have a lower C/N ratio and higher concentrations of N and phosphorus (P) (Vance 2000). Primary and secondary sludges are usually mixed, a polymer is added, and the mixed PMS is dewatered to a 25–40% dry solid content (Monte et al. 2009). Finally, the PMS can be hygienised through methods such as composting or lime stabilisation before being used as a fertiliser or soil amendment.

The addition of PMS with a high C/N ratio can induce N immobilisation by soil microbes and may have the potential to reduce N leaching (Aitken et al. 1998, Vinten et al. 1998, Busscher et al. 1999, Kirchmann and Bergström 2003). Besides N leaching, PMS additions have been shown to increase soil organic C content (Phillips et al. 1997, Rantala et al. 1999, Zibilske et al. 2000, Foley and Cooperband 2002, Chow et al. 2003). A decrease in soil organic matter content is currently one of the most significant threats to soils and leads to an increased risk of erosion (Jankauskas et al. 2007, Soinne et al. 2016) and nutrient leaching (Stoate et al. 2001). In fact, PMSs reportedly help in reducing the erosion and P losses from clay soils (Muukkonen et al. 2009, Rasa et al. 2021) and improving water retention capacity in coarse-textured soils (Räty et al. 2023). However, in contrast to several other studies, Vagstad et al. (2001) found an increase in residual mineral N in soil, and Gallardo et al. (2016) found an increase in NO_3^-–N concentration in leachate after PMS application, which increases the risk of N leaching.

Studies on the effects of mixed PMSs and especially lime-stabilised mixed pulp mill sludges (LPMS) on the N-leaching decreasing potential in agriculture are scarce. Comparisons of the potential of LPMS and composted mixed pulp mill sludges (CPMS) to decrease the amount of mineral N are also lacking. In this study, our main objective was to test the potential of LPMS and CPMS to reduce the concentration of mineral N in the soil, and thus potentially reduce N leaching in field conditions. A second objective was to investigate the mineralisation and immobilisation patterns of N from the PMSs in optimal conditions to better understand the mechanisms of the PMSs for influencing mineral N concentration in soil. Our first hypothesis was that PMSs would reduce soil mineral-N concentration through microbial N immobilisation, and thus reduce the N leaching potential. Our second hypothesis was that LPMS and CPMS have different effects on the N leaching potential due to their differing chemical compositions, especially regarding the amount of readily available C.

Materials and methods

Pulp mill sludges used in the laboratory incubation

In the incubation experiment, we used two mixed PMS products (manufactured by Soilfood Oy, formerly Tyynelän maanparannus Oy): a CPMS and a LPMS. CPMS came from the Stora Enso Imatra mill and LPMS from the MM Kotkamills Kotka mill. The PMSs were a mixture of primary and secondary sludge from the wastewater treatment of the pulp mills, consisting of approximately 70% primary sludge and 30% secondary sludge. The composting time for the static pile was eight weeks to meet the hygiene requirements for CPMS. For LPMS, lime stabilisation was performed by mixing burnt lime (CaO) and slaked lime ($Ca(OH)_2$) in the amount of 5% (fresh weight) of the PMS mass to raise the pH to 12 for at least two hours, which is required by the Finnish fertiliser regulation (Fertiliser regulation 964/2023). The pH of the PMS was 8.0 and 7.8, the C/N ratio was 21 and 36, the total C content was 45% and 38% on a dry weight basis, and the amount of soluble N was 0.45 and 1.4 g kg^{-1} for CPMS and LPMS, respectively (Appendix 1).

Pulp mill sludges used in the field experiment

In the field experiment, we used four types of mixed PMS products (manufactured by Soilfood Oy, formerly Tyynelän maanparannus Oy): two types of CPMS and two types of LPMS. One CPMS and one LPMS came from the Stora Enso Imatra mill (mill A), while the other CPMS and LPMS came from the UPM Lappeenranta mill (mill B), both located in southeastern Finland. The PMSs were a mixture of primary sludge (approx. 70%) and secondary sludge (approx. 30%) from the wastewater treatment of the pulp mills. The same hygienisation methods were used as used on the PMS of the incubation experiment mentioned above. Mill B sludges (CPMS B and LPMS B) had higher soluble N concentrations (1.60 and 1.10 g kg^{-1}) than mill A sludges (CPMS A and LPMS A, 0.69 and 0.63 g kg^{-1}) (Appendix 2). The pH of the PMSs ranged from 6.3 to 8.3, the C/N ratio from 22 to 32 and the total C content from 30% to 37% on a dry weight basis (Appendix 2). The Cd concentration in mill B sludges exceeded 1.5 mg kg^{-1} DM, which is the maximum allowable Cd concentration for soil amendments under Finnish law (Fertiliser regulation 964/2023).

Incubation study on soil respiration and nitrogen mineralisation

To determine the effects of PMSs on soil respiration and potential net N mineralisation, an incubation study was conducted under laboratory conditions from December 2018 to March 2019. The methods were similar to those described in Soinne et al. (2021). The incubation study had a randomised design with five fertilisation treatments: a CPMS treatment, a LPMS treatment, a treatment with a mineral fertiliser YaraMila Pellon Y3 23-3-8 (Kemira GrowHow, Helsinki, Finland) with 13% NH_4^+-N and 10% NO_3^--N (23% total N), a treatment with an organic meat and bone meal-based fertiliser Agra 844 (Ecolan Oy Nokia, Finland, N total 8.3%, C total 39.6%, C/N ratio 4.8) and a control without any fertiliser. The soil was a mixture of a sandy clay (1/3 of the mixture) and fine sand (particle size 0.2–0.6 mm, 2/3 of the mixture) classified according to Finnish soil classification (Aaltonen and Vuorinen 1949), and, prior to incubation, the soil was passed through a < 5-mm sieve. The mixed soil had a total C content of 2.4%, a pH of 6.2, a total N content of 0.25%, NO_3^--N content of 38 mg kg^{-1}, NH_4-N content of 0.5 mg kg^{-1} and P content of 3.3 mg kg^{-1} (Appendix 3).

For soil respiration determination, 100 g (dry matter, DM) of soil material was weighed into a 500-ml infusion bottle. For N mineralisation determination, separate samples were prepared with 100 g (DM) of soil material weighed into a 250-ml plastic cup. The fertilisers, including CPMS, LPMS, the mineral fertiliser and Agra 844, were ground and weighed into the bottle or cup so that each fertiliser treatment received 10 mg of total N, equivalent to 100 mg N kg^{-1} soil. Soil moisture was adjusted to 50% of the water holding capacity (WHC) of each soil–fertiliser combination and kept at that level throughout the experiment. A funnel method was used to measure the WHC of each soil–fertiliser combination: 20 g of soil material (DM) was placed into a funnel lined with filter paper, saturated with water for 1 hour before being allowed to drain freely for 24 hours. Each fertiliser treatment had four replicates for both soil respiration and N mineralisation. The infusion bottles for soil respiration and the plastic cups for N mineralisation were loosely covered with aluminium foil and incubated at 20 °C in the dark for 93 and 96 days, respectively.

Soil respiration and nitrous oxide (N_2O) release were measured from all infusion bottles on days 0, 1, 3, 6, 9, 12, 15, 21, 27, 42, 63 and 93. Before sampling, the incubation bottles were aerated with compressed air and then sealed with a chlorobutyl septum for 24 hours. Background concentrations of CO_2 and N_2O were measured from an infusion bottle that was incubated without soil or fertiliser. Twenty millilitre gas samples were taken from the headspace of the bottle with a hypodermic needle inserted through the septum. The gas sample was then filled into 12-ml Exetainer® vials, which were flushed with helium (He) and evacuated. The CO_2 and N_2O concentrations of the gas samples were measured using a gas chromatograph (7890A, Agilent Technologies, California, USA) equipped with a flame ionisation detector (FID) and a methaniser for CO_2 and CH_4, and an electron capture detector (ECD) for N_2O (Pihlatie et al. 2013). Background concentrations were subtracted from the concentrations in the bottles containing soil. For each sampling time, the respiration rate was calculated as CO_2-C and N_2O-N mg per kg soil dry weight (dry matter, oven-dried at 105 °C) per day. Cumulative respiration and N_2O release between sampling dates were calculated assuming linear changes in fluxes between measurement days.

Determination of N mineralisation was done on days 0, 1, 3, 9, 18, 48 and 96 after the start of incubation. Different samples were used for the determination each time (i.e., the entire contents of the cup were used for the determination). Concentrations of NH_4^+-N and (NO_3^- + NO_2^-)N were determined from 1:5 water extractions according to the standard SFS-EN 13652 (Finnish Standards Association 2002). As the amount of NO_2^- in the soil is very low, only NO_3^- is considered in this article.

Field experiment

The field experiment was set up in autumn 2015 on the Viikki research fields of the University of Helsinki, Finland (60° 13′ 21.9″ N 25° 00′ 41.2″ E). During the following two growing seasons (May to September 2016 and 2017), total precipitation was 320.5 and 274.9 mm, respectively. The average monthly air temperatures (°C) during the growing seasons were 14.2, 15.4, 17.8, 16.2 and 13.0 in 2016 and 9.8, 13.7, 16.0, 16.2 and 11.8 in 2017. The soil type was sandy clay with 10.8% organic matter (loss on ignition). The soil pH (H_2O) was 6.2 and the soil test P, K and Mg (acid ammonium acetate extraction, pH 4.65; Vuorinen and Mäkitie 1955) were 7.1 mg l^{-1}, 265 mg l^{-1} and 257 mg l^{-1}, respectively. According to the Finnish soil fertility classification, the P and K status of the soil were satisfactory and the Mg status poor.

The field experiment was a factorial design with crop type as the main plot factor and fertiliser treatment as the subplot factor (Fig. 1). The three levels of the main plot factor were spring cereals alone, spring cereals undersown with Italian ryegrass (*Lolium multiflorum*, variety ‘Meroa,’ Departement voor lantengenetica en veredeling, Melle, Belgium) and Italian ryegrass as a catch crop (Fig. 1).

Fig. 1. Experimental set-up with four replicate blocks (1–4), crop type as a main plot factor, and fertilisation treatment as a subplot factor. CPMS = composted pulp mill sludge, LPMS = lime-stabilised pulp mill sludge, A = Stora Enso Imatra mill, B = UPM Lappeenranta mill, C= Control, no fertilisation, M = Mineral fertiliser. Catch crop = catch crop Italian ryegrass after spring cereal, Spring cereal = spring cereal alone, Under sown = spring cereal undersown with Italian ryegrass

In the undersown plots, Italian ryegrass was sown with wheat in spring 2015 and tilled with a disc harrow into the soil in autumn 2015. Some of the Italian ryegrass was still growing the next winter. The Italian ryegrass in the catch crop plots was sown in autumn 2015 and tilled into the soil in spring 2016. The Italian ryegrass in the catch crop plots did not germinate successfully. The main plots were 15 m × 10 m in size. They were grouped into four complete blocks, and the levels of the main plot factor were randomised within the blocks. The subplot factor, fertiliser treatment, had six levels: two CPMS (A and B) and two LPMS (A and B) treatments with additional mineral fertilisation, a mineral fertiliser treatment and a control treatment without PMS or mineral fertiliser. Fertiliser treatments were randomly arranged in subplots of 2.2 m × 10.0 m within each main plot (Fig. 1). The treatments (6 × 3 = 18) were factorial combinations of the two factors, i.e., fertiliser treatment and crop type. Wheat (variety 'Anniina', Boreal Plant Breeding Ltd, Jokioinen, Finland) was grown in 2016 and oats (variety 'Obelix', Saatzucht Bauer GmbH & Co. KG, Obertraubling, Germany) in 2017. Due to uneven germination of the first sowing, the oats were sown again.

The PMSs were applied once in September 2015. The PMSs were first applied to the soil surface and then mixed into the top 10 cm of soil with a disc cultivator. No PMSs were applied in 2016 and 2017. PMS application rates ranged from 17.7 to 25.3 t ha^{-1} on a dry weight basis (Table 1). These rates were based on the maximum quantity (30 kg N ha^{-1}) of soluble N that may be applied in Finland in autumn according to nitrate fertilisation regulation. The quantity of soluble N applied in PMS treatment A was 15 and 17 kg ha^{-1} for LPMS and CPMS, respectively, and approximately 28 kg ha^{-1} in PMS treatment B (Table 2). A smaller quantity of soluble N was applied than planned because the exact nutrient content of the sludge was not known until after application. The total N applied varied due to the different total N content of the PMSs (Table 2). The amount of other nutrients applied also varied between the PMS treatments (Table 2). The mineral fertiliser used in the experiment was Kevätviljan Hiven Y, N-P-K: 20-3-8 (Kemira GrowHow, Helsinki, Finland) with 11.2% NH_4^+-N and 8.8% NO_3^--N. All PMS treatments received 50 kg N ha^{-1} from the mineral fertiliser (250 kg ha^{-1} fertiliser applied) in spring 2016 and 80 kg N ha^{-1} (400 kg ha^{-1} fertiliser applied) in spring 2017 (Table 1). The mineral fertiliser treatment received 80 kg N ha^{-1} (400 kg ha^{-1} fertiliser applied) in spring 2016 and 80 kg N ha^{-1} (400 kg ha^{-1} fertiliser applied) in spring 2017 (Table 1). Specific crop recommendations were followed when applying herbicides during both years. Soil samples were collected on 29 September 2015, 22 October 2015, 15 November 2015, 22 April 2016, 12 September 2016 and 21 October 2017 from a depth of 0–20 cm using a hand auger (diameter 2 cm).

Table 1. The application rates of the pulp mill sludges (autumn 2015) and mineral fertiliser (spring 2016 and 2017) for each fertiliser treatment (kg ha^{-1} on a dry weight basis). The mineral fertiliser was Kevätviljan Hiven Y, N-P-K: 20-3-8 (Kemira GrowHow, Helsinki, Finland).

	Autumn 2015	Spring 2016	Spring 2017
Treatment	Pulp mill sludges	Mineral fertiliser	Mineral fertiliser
CPMS A	24864	250	400
LPMS A	24326	250	400
CPMS B	17661	250	400
LPMS A	25324	250	400
Control	-	-	-
Mineral	-	400	400

CPMS = composted pulp mill sludge; LPMS = lime-stabilised pulp mill sludge; A = Stora Enso Imatra mill; B = UPM Lappeenranta mill; Control = no fertilisation; Mineral = mineral fertilisation

Table 2. The amount of nutrients applied in the pulp mill sludges in the four PMS types of the field experiment (kg ha^{-1} on a dry weight basis)

	CPMS A	LPMS A	CPMS B	LPMS B
N total	298	231	230	355
N soluble	17	15	28	28
P	50	46	27	73
K	18.6	17.0	4.9	9.4
S	164	131	136	233
B	0.5	0.3	0.2	0.4
Mn	39.8	23.8	23.0	45.6
Ca	1119	1800	618	2406
Ctot	8180	7395	6464	7901

CPMS = composted pulp mill sludge, LPMS = lime-stabilised pulp mill sludge; A = Stora Enso Imatra mill; B = UPM Lappeenranta mill

Ten subsamples were taken from each plot and combined into one pooled sample. The soil samples were placed in a freezer (–20 °C) and kept there until analysis. NH_4^+-N and NO_3^--N contents were determined from 2 M 1:5 potassium chloride (KCl) extractions according to SFS-EN ISO 11732:2005 and SFS-EN ISO 13395-1:1997 (Finnish Standards Association 2005, 1997), respectively.

Statistical analyses

The effects of the fertiliser treatments (CPMS, LPMS, Agra 844, mineral and control) on N mineralisation and soil respiration in the incubation study were analysed using linear mixed models (the entire data) and linear models (each measurement time point separately). Fertiliser treatment was used as a fixed effect. Measuring day was included as a random factor in the linear mixed models. Models were fitted using the lmer function of the R package lme4 (Bates et al. 2015) and the lm function of the R package stats (R Core Team 2021). Tukey's post-hoc pairwise comparisons were performed to compare the treatments with each other. Treatment effects with probability values above 0.05 were considered nonsignificant. The effects of the fertiliser treatments (two CPMSs, two LPMSs, mineral and control) and crop type (spring cereal alone, spring cereal with undersown ryegrass and spring cereal with catch crop ryegrass) on soil NO_3^--N concentration in the field experiment were investigated using analysis of variance (ANOVA). The analysis was followed with a split-plot ANOVA with crop type as the main plot factor and fertiliser treatment as the subplot factor. The models were fitted with the function sp.plot of the R package agricolae (de Mendiburu 2021). Least significant difference (LSD) tests were performed using the LSD.test function of the agricolae package to compare each fertilisation and crop type treatment with one another. The statistical analysis of the second measuring time was executed without one of the soil samples from the CPMS B treatment, which had exceptionally high NH_4^+-N and NO_3^--N concentrations. Treatment effects with probability values above 0.05 were considered nonsignificant.

Results

Effects of PMSs on concentration of mineral N and soil respiration in the incubation experiment

For both types of PMSs, the NH_4^+-N concentration in the soil was significantly lower compared to the mineral fertiliser treatment at the beginning of the experiment (days 0–18) (Table 3). Also, at the first four measurement time points (days 0, 1, 3 and 9), both PMSs had significantly less NH_4^+-N in the soil than recorded in Agra 844. On day 48, LPMS had more NH_4^+-N in the soil than recorded in the CPMS, Agra 844 or control treatment. No significant differences in NH_4^+-N concentration were observed in the soil between the two PMS types, except on day 48. At the end of the experiment, no statistically significant differences between any of the treatments were detected.

Table 3. Soil NH_4^+–N and NO_3^-–N (mg kg^{-1} soil dry matter) concentrations during 96 days of incubation at 20 °C. Average ± standard error (SE), n = 4

Treatment	NH_4^+-N						
	0 d	1 d	3 d	9 d	18 d	48 d	96 d
CPMS	1.1±0.1 c	1.9±0.3 bc	2.0±0.3 c	0.5±0.0 c	0.5±0.0 b	0.4±0.0 b	0.5±0.0 a
LPMS	0.4±0.1 c	1.3±0.1 c	0.6±0.0 c	0.3±0.1 c	0.4±0.1 b	0.9±0.1 a	0.9±0.1 a
Agra 844	3.5±0.6 b	4.9±0.4 b	12.8±1.4 b	12.1±1.5 b	0.9±0.2 b	0.2±0.0 b	0.3±0.2 a
Control	0.7±0.0 c	1.2±0.0 c	1.6±0.0 c	0.4±0.1 c	0.3±0.0 b	0.3±0.2 b	0.3±0.1 a
Mineral	23.3±1.0 a	25.0±1.6 a	25.3±0.9 a	18.8±0.8 a	3.7±0.3 a	0.6±0.1 ab	0.3±0.1 a
	NO_3^-–N						
CPMS	39.8±1.6 b	40.0±1.4 bc	44.8±1.3 b	54.3±0.5 c	61.0±0.9 c	62.0±1.3 c	65.3±1.4 c
LPMS	42.5±1.4 b	42.5±1.2 bc	46.8±0.9 b	8.4±2.8 d	3.2±0.3 d	8.4±0.4 d	26.3±0.3 d
Agra 844	41.8±2.8 b	45.0±1.2 b	48.3±2.1 b	68.3±1.9 b	107.5±2.5 b	122.5±2.5 b	132.5±2.5 b
Control	41.0±1.0 b	37.0±0.4 c	42.8±1.2 b	54.3±1.0 c	58.3±1.3 c	62.0±1.2 c	69.8±0.9 c
Mineral	96.5±0.9 a	104.8±3.0 a	105.0±2.9 a	125.0±2.9 a	152.5±2.5 a	170.0±0.0 a	175.0±5.0 a

Letters indicate significant differences ($p < 0.05$) in the NH_4^+–N or NO_3^-–N concentrations between the fertilisation treatments on each measurement day. CPMS = composted pulp mill sludge; LPMS = lime-stabilised pulp mill sludge; Agra 844 = an organic meat and bone meal-based fertiliser; Control = no fertilisation; Mineral = mineral fertiliser

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https://doi.org/10.23986/afsci.142012

In general, all fertiliser treatments showed much lower NH_4^+-N concentrations than NO_3^--N concentrations. For both PMS types, the NO_3^--N concentration in the soil was significantly lower compared to the mineral fertiliser treatment at all measurement times during the 96-day laboratory incubation (Table 3). Also, after the first three measurement time points (days 0, 1 and 3), both PMSs had significantly less NO_3^--N in the soil than Agra 844 until the end of the laboratory incubation. From day 9 until the end of incubation, LPMS had less NO_3^--N in the soil than the control. During the first three measurement time points (days 0, 1 and 3), we observed no significant differences in NO_3^--N concentration in the soil between the two PMS types. Thereafter, LPMS had a significantly lower soil NO_3^--N concentration than the CPMS (Table 3).

For both PMS types, the soluble inorganic N concentration in the soil was significantly lower compared to the mineral fertiliser treatment during the whole 96-day incubation period (Fig. 2). Also, after the first two measurement time points (days 0 and 1), both PMSs had significantly less soluble inorganic N in the soil than the Agra 844 treatment until the end of the laboratory incubation. We observed no significant differences in soil soluble inorganic N concentration between the two PMS types during the first three measurement time points (days 0, 1 and 3). Thereafter, LPMS had a significantly lower soil soluble N concentration than CPMS (Fig. 2).

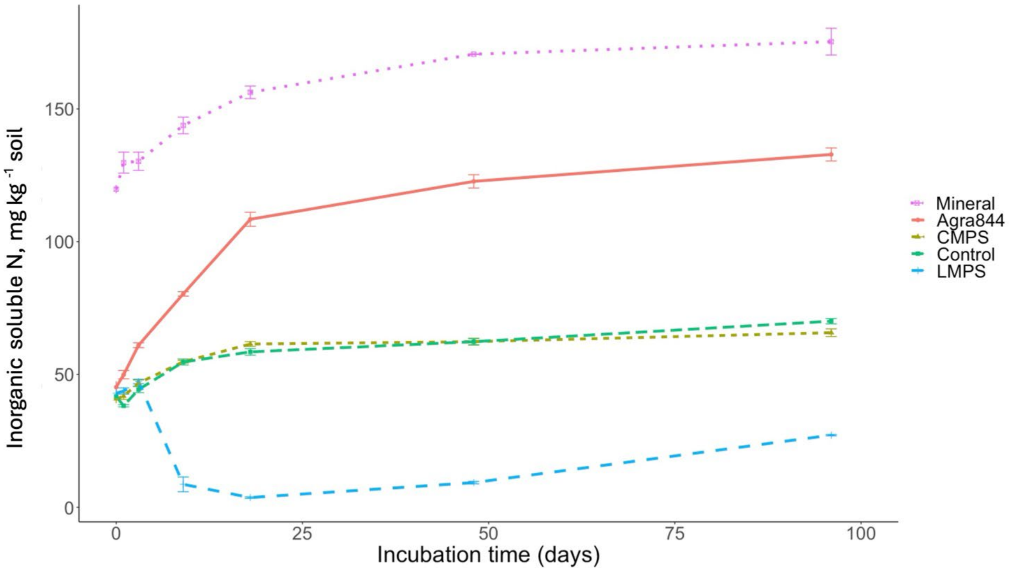

Fig. 2. Concentration of soil inorganic soluble N (NO_2^--N + NO_3^--N + NH_4^+-N) (mg kg^{-1} soil dry weight basis) during 96 days of incubation at 20 °C for five fertiliser treatments (n = 4). Average ± standard error (SE). CPMS = composted pulp mill sludge, LPMS = lime-stabilised pulp mill sludge, Agra 844 = an organic meat bone meal-based fertiliser, Mineral = mineral fertiliser.

The soil respiration rate of LPMS was significantly higher compared to the other treatments almost throughout the incubation (Table 4). CPMS had a significantly higher soil respiration rate compared to the mineral fertiliser treatment on days 0, 1, 15, 21, 42, 63 and 93. In contrast, CPMS had a significantly lower soil respiration rate compared to Agra 844 on the first two measuring days but a higher rate at the end of the experiment (days 42–93).

Table 4. Soil CO_2-C release (µg g^{-1} soil day^{-1}) and cumulative CO_2-C release during 93 days of incubation at 20 °C. Soil CO_2-C release: average ± standard error (SE), n = 4

Treatment	0 d	1 d	3 d	6 d	9 d	12 d	15 d	21 d	27 d	42 d	63 d	93 d	Cumulative CO_2–C release (µg g^{-1} soil)
CPMS	26.6±0.4c	37.0±0.9c	8.8±0.2bc	6.7±0.3bc	4.4±0.1bc	4.5±0.2b	4.1±0.1b	3.8±0.1b	4.2±0.1ab	5.6±0.6b	7.1±2.3a	3.7±0.3a	577b
LPMS	84.1±2.9a	122.7±4.9a	139.9±15.6a	99.8±3.8a	34.9±1.2a	19.2±1.3a	16.8±0.4a	11.6±0.5a	7.5±2.6a	8.0±0.2a	6.2±0.1ab	4.1±0.2a	1737a
Agra 844	35.6±0.6b	74.7±2.3b	37.7±1.5b	13.9±0.6b	6.5±0.2b	4.9±0.2b	4.4±0.1b	3.3±0.0b	2.2±0.7b	2.3±0.1c	1.9±0.1bc	1.5±0.1b	492b
Mineral	19.5±0.7d	24.5±0.8d	5.8±0.3c	4.3±0.1c	2.8±0.1c	2.4±0.1b	2.2±0.1c	1.8±0.1c	1.7±0.1b	1.3±0.1c	1.2±0.1c	1.1±0.1b	211c
Control	17.3±0.4d	25.1±0.7d	6.8±0.3c	4.5±0.1c	3.1±0.1c	2.8±0.1b	2.7±0.1c	2.3±0.1c	2.0±0.0b	1.7±0.1c	1.7±0.0c	1.5±0.1b	249c

Different letters indicate significant differences ($p< 0.05$) between the treatments on a measurement day or in cumulative CO_2-C release. CPMS = composted pulp mill sludge; LPMS = lime-stabilised pulp mill sludge; Agra 844 = an organic meat and bone meal-based fertiliser; Control = no fertilisation; Mineral = mineral fertiliser

The cumulative amount of CO_2-C released over 93 days was highest with the LPMS treatment and lowest with the mineral fertiliser treatment and the control treatment (Table 4). CO_2-C released from the total C added was higher for LPMS (37.5% of added C) than for CPMS (15.9% of added C). In comparison, CO_2-C released from the total C added was significantly lower for both PMSs than for Agra 844 (46.8% of added C).

Cumulative N_2O-N release was highest for Agra 844 (0.63 mg N_2O-N kg^{-1} soil). CPMS and LPMS both had a release of 0.04, and the mineral fertiliser and control treatments had releases of 0.05 and 0.01 mg N_2O-N kg^{-1} soil. N_2O-N release as a proportion of added N was less than 0.0% with all fertiliser treatments.

Effects of PMSs on soil NO_3^-–N concentration in the field experiment

The soil NO_3^--N concentration was significantly lower for all four PMSs compared to the mineral fertilisation and the control treatments at all three measurement times in autumn 2015 after PMS application (Fig. 3A). In the following spring, the soil NO_3^--N concentration was significantly lower with three out of four PMSs compared to the mineral fertiliser and control treatments. The soil NO_3^--N concentration was significantly higher with CPMS A than with LPMS A and CPMS B.

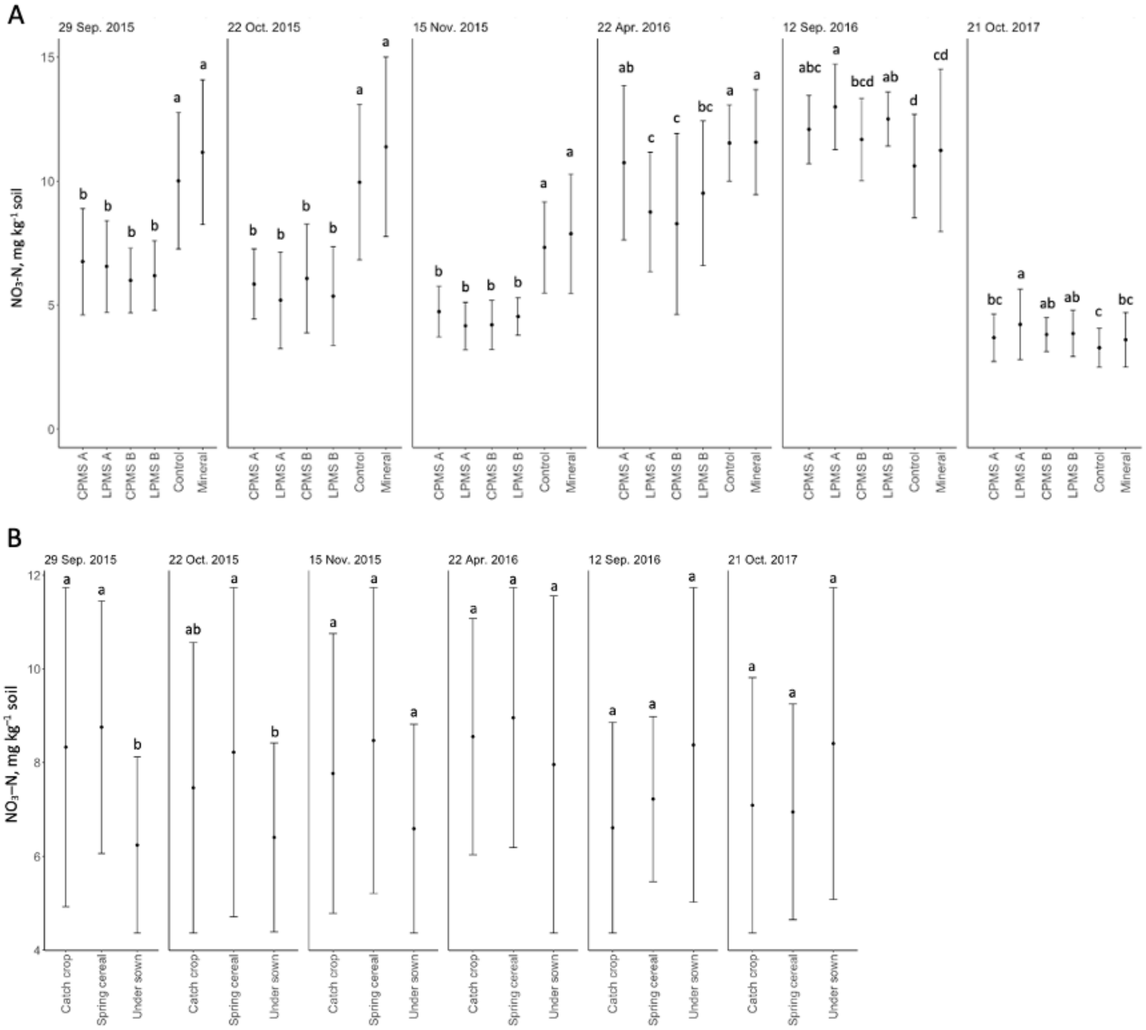

Fig. 3. NO_3^--N concentrations (mg kg^{-1} soil dry matter) in soil during the two–year field experiment in six fertiliser treatments (A; n = 24) and three crop types (B; n = 12). Average ± standard error (SE). Statistically significant differences between the treatments are indicated by different letters above the bars ($p < 0.05$, Tukey's test). CPMS = composted pulp mill sludge, LPMS = lime-stabilised pulp mill sludge, Control = no fertilisation, Mineral = mineral fertiliser. A = Stora Enso Imatra mill, B = UPM Lappeenranta mill. Catch crop = catch crop Italian ryegrass after spring cereal, Spring cereal = spring cereal alone, Under sown = spring cereal undersown with Italian ryegrass

In autumn 2016, one year after PMS application, LPMS A and LPMS B had significantly higher soil NO_3^--N concentrations than the mineral fertiliser treatment. In addition, three out of four PMSs had higher soil NO_3^--N concentrations than the control treatment. Also, CPMS B had significantly less NO_3^--N in the soil than LPMS A in autumn 2016. In autumn 2017, two years after PMS application, LPMS A had a significantly higher soil NO_3^--N concentration than the mineral fertilisation treatment. In addition, three out of four PMSs had significantly higher soil NO_3^--N concentrations than the control. LPMS A had significantly higher soil NO_3^-–N concentration than the CPMS A treatment in autumn 2017. The interaction between the PMSs and the crop type was not statistically significant.

Spring cereal undersown with Italian ryegrass had significantly less NO_3^--N in the soil than spring cereal alone and catch crop Italian ryegrass at the first measuring time during the first autumn after PMS application (Fig. 3B). At the second measurement time point during the first autumn, spring cereal undersown with ryegrass had significantly less NO_3^--N in the soil than spring cereal alone. Thereafter, no significant differences were observed in soil NO_3^--N concentration between the crop types.

Discussion

PMSs potential to reduce mineral N concentration in the soil

Our study tested the potential of LPMS and CPMS to reduce mineral N concentration in the soil, and thus the risk of N leaching from arable land. Based on the laboratory incubation experiment and the field experiment, adding PMSs to soil results in microbial immobilisation of nutrients, and thus has the potential to temporarily reduce the concentration of mineral N in the soil, which was in line with our first hypothesis. The second hypothesis on the differences between LPMS and CPMS was supported by the incubation experiment, where adding LPMS immobilised more N than the addition of CPMS. However, no consistent differences between the PMS types were found in the field experiment.

N immobilisation potential in laboratory conditions

Soil NO_3^--N and inorganic soluble N concentrations were lower in the laboratory incubation with both PMS treatments than with the mineral fertiliser treatment due to the lower N solubility in the PMSs compared to mineral fertilisation. As N_2O-N release was minimal with both PMSs, no gaseous N losses can be assumed. Soil NH_4^+-N concentrations were lower with both PMS types than with the mineral fertiliser treatment on days 0–18 of incubation, but no differences were found between the treatments at the end of incubation when NH_4^+-N was already nitrified. Lower concentrations of soluble inorganic N in soil with LPMS than with CPMS, starting from the fourth measurement time point (day 9), could be due to the lower C/N ratio of CPMS (21) than LPMS (36), as the decomposition of organic matter with a high C/N ratio may initially lead to a net immobilisation of N (Mary et al. 1996). Previous studies have found that organic matter with a C/N ratio higher than 25 leads to a net immobilisation of N in the soil (Trinsoutrot et al. 2000, Paul 2007). Besides the C/N ratio, other substrate properties, such as soluble C, cellulose, lignin and polyphenol content, may determine whether net mineralisation or net immobilisation of N occurs (Fog 1988).

CPMS had similar inorganic soluble N concentrations in soil than the control with no fertilisation, indicating that N was mineralised slowly from CPMS. This is in line with other studies that have shown that N is mineralised slowly even when compost is rich in N (Hartz et al. 2000, Nevens and Reheul 2003, Zaman et al. 2004, Masunga et al. 2016). This is probably because composting stabilises the organic compounds and reduces the proportion of easily available forms of C and N (Flavel and Murphy 2006, Hubbe et al. 2010). Indeed, the soluble N content of CPMS was lower than that of LPMS (0.5 and 1.4 g kg^{-1}). After the first three measurement time points (days 0, 1 and 3), LPMS had significantly less inorganic soluble N in the soil than the other fertiliser treatments and the control without fertiliser throughout the experiment. Other studies have also found that PMS use can increase or decrease the soluble N concentration in the soil, depending at least partly on the C/N ratio of the product: Kirchmann and Bergström (2003) found that primary fibre sludge and de-inked fibre sludge with C/N ratios of 130 and 117, respectively, decreased the inorganic N concentration in the soil during a 27-day incubation period at 5 °C after the addition of mineral fertiliser, while secondary sludge with a C/N ratio of 6 did not. Hamnér and Kirchmann (2005) also found that primary PMS with a C/N ratio of 130 decreased the inorganic concentration in the soil. In contrast, Gallardo et al. (2016) found an increase in NO_3^-–N concentration in leachate after sludge application (C/N ratio not mentioned), compared to untreated controls.

LPMS had the highest CO_2-C release on almost every measurement day of the incubation compared to the other treatments. As a proportion of total added C, LPMS released more CO_2-C than CPMS (15.9% for CPMS and 37.5% for LPMS). A high CO_2-C release indicates high microbial activity, which may lead to N immobilisation when C/N ratio of the organic matter is high (Janssen 1996). This is supported by our findings that LPMS had lower concentrations of soluble inorganic N in soil than CPMS, starting from day 9 of the incubation. CPMS had a lower C/N ratio than LPMS (21 and 36) resulting in a sufficient amount of N for microbes.

The rapid and high CO_2-C release from LPMS could be explained by a high concentration of the readily mineralisable C fraction in LPMS, as the mineralisation process of C is controlled by the type of organic matter added and on the labile C content (Smith et al. 2015). Also, LPMS contained more C than the other treatments, and thus more C ended up in the soil, affecting the CO_2-C release. Interestingly, CO_2-C release was still higher with both PMSs than with other fertiliser treatments or the control at the end of incubation.

As minimal or no net N mineralisation occurred from either PMS during the 96-day incubation under optimal conditions, PMSs applied in autumn can be assumed to decrease the concentration of soluble N in autumn and the following spring because the soil temperature in Finland is below 5 °C in winter and mineralisation is therefore slow (Troeh and Thompson 2005). On the other hand, the freeze-thaw process that occurs in winter in Finland can increase nitrification under field conditions (Song et al. 2017), which may increase the risk of N leaching. It is also possible that the N will mineralise after the incubation period. For example, Abbasi and Khaliq (2016) found that wheat straw residues (C/N ratio 46) decreased the NO_3^--N concentration in the soil until day 84, after which the NO_3^--N concentration increased to a maximum of 15.9 mg kg^{-1} on day 140.

Impact of PMSs on plant available and potentially leachable N in field conditions

In the field experiment, all PMSs reduced soil NO_3^--N concentrations during the first autumn and three out of four PMSs reduced the NO_3^--N concentration in the soil the next spring. The lower soil NO_3^--N concentrations observed in the PMS treatments than in the mineral fertiliser or the control treatments are probably due to immobilisation caused by the rather high C/N ratio of the PMSs (22–32 in our field experiment), as explained at the beginning of the discussion. All four PMSs reduced soil NO_3^--N concentrations by 26–48% during the first autumn after application and by 7–28% the following spring. In contrast, Karhu et al. (2021) found that ligneous fibre (a PMS) did not reduce cumulative NO_3^--N leaching measured during the 3.5-month growing season compared to the fertilised control.

LPMS A obtained the lowest amount of soluble N from the sludge. In addition, LPMS A had the highest C/N ratio (32) of the PMSs used in the field experiment and the N was therefore more likely immobilised by microbes. Interestingly, the soil NO_3^--N concentration with LPMS A was not significantly different from CPMS B and LPMS B, which had a lower C/N ratio and a higher amount of soluble N received from the sludge. However, the soil NO_3^--N concentration with LPMS A was significantly lower than with CPMS A, even though CPMS A had a similar C/N ratio and a similar amount of soluble N received with LPMS A. Also, the soil NO_3^--N concentration with LPMS B, which had the lowest C/N ratio, did not differ from other PMSs throughout the experiment. This suggests that the soil NO_3^--N concentration was influenced by other factor(s) than the C/N ratio and the amount of soluble N in the soil amendments.

PMSs with high C/N ratios can cause immobilisation of N, and if the immobilised N is not released fast enough for the plants to utilise the N, the subsequent crop may be affected negatively. However, according to our previous article, yields were not affected (Kinnula et al. 2020). In general, grain yields with the PMS treatments were as good as with the mineral fertiliser treatment and higher than with the control treatment one and two years after PMS application (Kinnula et al. 2020), indicating relatively good N availability to the crops in the PMS treatments. However, applying both types of PMS resulted in lower grain N content (Kinnula et al. 2020), indicating that the timing of N availability was not optimal. It is worth noting that the mineral fertiliser treatment did not receive fertiliser in autumn 2015 and was only fertilised in spring 2016 after soil NO_3^--N concentrations were measured. Although PMSs contained N, soil NO_3^--N concentrations before mineral fertilisation were lower with PMSs than with the mineral fertiliser or control treatments, which is another indication that the high C concentrations of PMSs caused N immobilisation.

One year after the PMS applications, in autumn 2016, some of the PMSs had higher soil NO_3^--N concentrations than the mineral fertiliser or the control treatment, indicating that the N immobilised by these PMSs was available again at this time. This can be explained by dying of the microbes when the easily available C is consumed, and the subsequent release of soluble N into the soil. The time at which immobilised nitrogen becomes

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https://doi.org/10.23986/afsci.142012

available again depends on environmental factors such as soil temperature and moisture (Parton et al. 2007) and the type of PMSs. Ideally, this mobilisation should take place the following spring or summer after the PMS has been applied the previous autumn so that the plants can use the available N. As all PMSs received additional mineral fertiliser to match the amount of soluble N added in received from the mineral fertiliser treatment, the higher NO_3^--N concentrations in the soil with some of the PMSs show that these PMSs were no longer able to cause N immobilisation one year after PMS applications. In autumn 2017, LPMS A still had a significantly higher NO_3^--N concentration in soil than the mineral fertilisation and the control treatments, indicating continuing N mineralisation. This result is similar with Aitken et al. (1998), who found that net N immobilisation occurred initially, after the application of de-inked PMS (C/N ratio 86). Subsequently, little or no net N immobilisation was detected for a certain period. By the third year after de-inked PMS application, they found an indication that the immobilised N was remineralised. Rasa et al. (2021) found no significant differences in NO_3^--N concentration in percolation water from CPMS- and LPMS-treated soil monoliths during the first three years of their field experiment. In the fourth year, LPMS treatment had a significantly higher NO_3^--N concentration in percolation water than the control, which is in accordance with our findings that LPMS use results in higher soil NO_3^--N concentrations some years after application. CPMS B having less NO_3^--N in the soil than LPMS A in autumn 2016 and CPMS A having less NO_3^--N in the soil than LPMS A in autumn 2017 is interesting because composting should stabilise C (i.e., there is less easily available C for microbes to use) and therefore N should be less immobilised with composted PMSs. It is also possible that if composting is performed in the short term without a long stabilisation period (PMSs used in our study were composted only eight weeks), stabilisation does not occur. Our findings are similar with the findings of Vagstad et al. (2001), who observed that composted PMS had less mineral N in the soil during the first year after sludge application than the other sludge types did, including LPMS.

The addition of high C/N organic amendments is likely to immobilise inorganic N, but Baggs et al. (2002) stated that a high input of organic C, which is readily available to microorganisms, can lead to increased denitrification in the soil, resulting in a reduction in soil NO_3^--N content. Vinten et al. (1998) reported increased N_2O emissions after PMS applications (mean C/N ratio 25), ploughed to a depth of 35 cm, and suggested that denitrification is an important mechanism for N loss, especially in the deep cultivation treatments. Our laboratory incubation did not confirm that denitrification was the cause of the decrease in inorganic N concentration, as we measured relatively low N_2O production in all amendments. Furthermore, in contrast to Vinten et al. (1998), the PMS in the field experiment was only mixed in the top 10 cm.

Undersowing spring cereals with Italian ryegrass reduced soil NO_3^--N concentrations during the first autumn 50 days after PMS application. During the following spring and the next two autumns, we observed no differences in soil NO_3^--N concentrations between the crop type treatments. This agrees with Känkänen and Eriksson (2007), who found that Italian ryegrass reduced soil NO_3^--N concentrations in late autumn but not during the next spring. In our field experiment, PMSs first immobilised N and later N was released back to the soluble N pool; thus, cover crops could be used to capture this released N when the risk for N leaching is high. Italian ryegrass as a catch crop did not reduce the NO_3^--N concentration in the soil compared to the ‘cereal alone’ crop type. This is probably due to the poor germination of Italian ryegrass during the autumn when it was sown. Aronsson and Torstensson (1998) found an increased risk of N leaching if the new catch crop does not establish well. However, despite the poor germination of the catch crop in our experiment, the soil NO_3^--N concentration did not increase during the first autumn or during the following years in the catch crop type compared to the ‘cereal alone’ crop type.

Conclusions

Our study shows that adding pulp mill sludges to soil results in decreased concentrations of soluble N, very likely caused by microbial immobilisation, and thus has the potential to temporarily reduce N leaching from arable land. The results of the incubation experiment indicate that both composted and lime-stabilised pulp mill sludges have the potential to cause net immobilisation of N, but immobilisation is higher with lime-stabilised pulp mill sludge than with composted pulp mill sludge. The results of the field experiment suggest that composted and lime-stabilised pulp mill sludges can reduce concentration of mineral N in the soil, and thus potentially decrease the leaching of N in a cold boreal climate during the first autumn and the next spring through temporary N immobilisation when applied to mineral agricultural soils with a high organic matter content. However, there was no clear pattern in the effect of pulp mill sludge type on soil NO_3^--N concentration in the field conditions, probably reflecting smaller differences in the chemical composition of the sludge types in the field experiment than in the incubation experiment, as well as the complexity of N dynamics in the soil. Undersown Italian ryegrass could be used to catch the N when pulp mill sludges no longer do so, that is one and two years after their application. Further laboratory experiments with longer incubation periods are needed to investigate the mineralisation patterns of N after the application of the pulp mill sludges. Also, further field experiments are needed to determine the optimal amount of pulp mill sludge that should be applied both to ensure optimal nutrient levels for the subsequent crop and to reduce the risk of nutrient leaching.

Acknowledgements

We thank Markku Tykkyläinen, who helped with the establishment and management of the field experiment. This work was supported by the Maa- ja vesitekniikan tuki ry, the Finnish Funding Agency for Technology and Innovation (Tekes, now Business Finland) as a part of the NSPPulp project, Stora Enso Oyj, UPM Oyj and by the Strategic Research Council (SRC) at the Research Council of Finland (grant number 352435).

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Appendices

Appendix 1. Chemical characteristics (expressed on a dry weight basis) of the composted pulp mill sludge (CPMS) and lime-stabilised pulp mill sludge (LPMS) used in the incubation experiment. *N soluble includes NO_3^--N, NH_4^+-N and dissolved organic N.

	CPMS	LPMS
Dry matter (%)	37.4	43.8
pHH_2O	8.0	7.8
C total, %	45.3	37.5
N total, g kg^{-1}	22	10
N soluble*, g kg^{-1}	0.45	1.4
C/N ratio	21	36
P total, g kg^{-1}	1.6	0.9
K, g k^{g-}1	0.51	0.39
Ca, g k^{g-}1	65	51
Mn, g kg^{-1}	0.6	0.1
Cd, mg kg^{-1}	0.37	0.43
Cu, mg kg^{-1}	18	17
Zn, mg kg^{-1}	69	320
Organic matter, %	72	70

Soluble N content was determined from 1:5 soil-to-solution water extractions according to SFS-EN 13652 (Finnish Standards Association 2002) and total N content by Kjeldahl digestion (Bremner and Mulvaney 1982). Total P, potassium (K), manganese (Mn), calcium (Ca), copper (Cu), zinc (Zn), and cadmium (Cd) contents were determined after acid digestion according to the standard SFS-EN ISO 11885:2009 (Finnish Standards Association 2009). The total C content of the PMSs was quantified by dry combustion using a Leco CN828 analyser (Leco Corp., St Joseph, MI, USA). The organic matter content was determined as loss on ignition at 550 °C for four hours (Finnish Standards Association 2000a). The pH was determined from 1:5 soil-to-solution water suspensions according to SFS-EN 13037 (Finnish Standards Association 2000b) and the dry matter gravimetrically according to SFS-EN 13040 (Finnish Standards Association 2000c).

Appendix 2. Chemical characteristics of the four pulp mill sludges used in the field experiment, on a dry weight basis. *N soluble includes NO_3^--N, NH_4^+-N and dissolved organic N. The same analytical methods were used to determine the chemical characteristics of the PMS as those used on the PMS of the incubation experiment mentioned above in Appendix 1.

	CPMS A	LPMS A	CPMS B	LPMS B
Dry matter (%)	48	47	41	50
pHH_2O	7.8	8.3	6.3	7.7
C total, %	32.9	30.4	36.6	31.2
N total, g kg^{-1}	12	9.5	13	14
N soluble*, g kg^{-1}	0.69	0.63	1.60	1.10
C/N ratio	27	32	28	22
P total, g kg^{-1}	2.0	1.9	1.5	2.9
K, g kg^{-1}	0.75	0.70	0.28	0.37
Ca, g kg^{-1}	45	74	35	95
Mn, g kg^{-1}	16	1	13	18
Zn, g kg^{-1}	0.1	0.1	0.2	0.2
Cu, mg kg^{-1}	25	17	15	19
Pb, mg kg^{-1}	8	8	8	8
Cd, mg kg^{-1}	0.6	0.5	2	2
Organic matter, %	74.5	68.8	83.1	71.5

CPMS = composted pulp mill sludge; LPMS = lime-stabilised pulp mill sludge; A = Stora Enso Imatra mill; B = UPM Lappeenranta mill; Lead (Pb) content was determined after acid digestion according to the standard SFS-EN ISO 11885:2009 (Finnish Standards Association 2009).

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https://doi.org/10.23986/afsci.142012

Appendix 3. Chemical characteristics of soil used in the laboratory incubation, on a dry weight basis.

C total, %	2.44
N total, %	0.25
NH_4^+-N soluble, mg kg^{-1}	0.5
NO_2^--N soluble, mg kg^{-1}	< 0.1
NO_3^--N, mg kg^{-1}	38
P soluble, mg kg^{-1}	3.3
P total, mg kg^{-1}	900
pHH_2O	6.2

NO_3^--N, NH_4^+-N and P were determined from 1:5 water extractions according to the standard SFS-EN 13652 (Finnish Standards Association 2002) and total P after acid digestion according to the standard SFS-EN ISO 11885:2009 (Finnish Standards Association 2009). Total C and N contents of the soil and Agra 844 fertiliser were determined by dry combustion using a Leco CN828 analyser (Leco Corp., St Joseph, MI, USA).