The Effect of Phosphogypsum on Greenhouse Gas Emissions during Cattle Manure Composting

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ABSTRACT

Phosphogypsum (PG), a by-product of the phosphate fertilizer industry, reduces N losses when added to composting livestock manure, but its impact on greenhouse gas emissions is unclear. The objective of this research was to assess the effects of PG addition on greenhouse gas emissions during cattle feedlot manure composting. Sand was used as a filler material for comparison. The seven treatments were PG10, PG20, PG30, S10, S20, and S30, representing the rate of PG or sand addition at 10, 20, or 30% of manure dry weight and a check treatment (no PG or sand) with three replications. The manure treatments were composted in open windrows and turned five times during a 134-d period. Addition of PG significantly increased electrical conductivity (EC) and decreased pH in the final compost. Total carbon (TC), total nitrogen (TN), and mineral nitrogen contents in the final composted product were not affected by the addition of PG or sand. From 40 to 54% of initial TC was lost during composting, mostly as CO_2, with CH_4 accounting for $<14\%$. The addition of PG significantly reduced CH_4 emissions, which decreased exponentially with the compost total sulfur (TS) content. The emission of N_2O accounted for $<0.2\%$ of initial TN in the manure, increasing as compost pH decreased from alkaline to near neutral. Based on the total greenhouse gas budget, PG addition reduced greenhouse gas emissions (CO_2–C equivalent) during composting of livestock manure by at least 58%, primarily due to reduced CH_4 emission.

Composting is an alternative to traditional manure management and is increasingly being adopted by the beef feedlot industry in Alberta, Canada. Studies have shown that various greenhouse gases (GHGs) are emitted during composting (Hao et al., 2001, 2004), depending on factors such as C and N content in manure, aeration, and amendment additions (Al-Kanani et al., 1992; Mahimairaja et al., 1994; Lopez-Real and Baptista, 1996; Swinker et al., 1998; Shi et al., 1999; Osada et al., 2000).

Phosphogypsum (PG) is a by-product of phosphorus fertilizer production, consisting primarily of gypsum ($CaSO_4{\cdot}2H_2O$). Currently, Alberta has large stockpiles of the material in storage. Larney et al. (2000, 2001) reported that a PG–cattle manure mixture has higher mineral nitrogen ($NH_4^+ + NO_3^-$) content than cattle manure alone after three months of active composting. The mineral N content in the straw-bedded cattle manure compost almost tripled following the addition of 20% PG (on a manure dry weight basis) compared with that without the PG addition. This was attributed to a decrease in compost pH. In addition, PG enhanced the sulfur (S) content of the compost.

Changes in manure or compost pH, mineral N, and S content may affect greenhouse gas emission during composting. Decreases in pH have been reported to either decrease (Muller et al., 1980) or increase (Stevens and Laughlin, 1998) N_2O production and emission from soils. Others reported maximum N_2O emission fluxes from soil near neutral or slightly acid ($pH = 6.5$) conditions (Stevens et al., 1998). Similarly, CH_4 production activity of methanogens usually peaks around neutral or slightly alkaline conditions (Garcia et al., 2000) and is more sensitive to changes in soil pH than methanotrophic CH_4 oxidation (Dunfield et al., 1993; Wang et al., 1993).

High emissions of N_2O are associated with high levels of NH_4^+ during nitrification under aerobic conditions and high levels of NO_3 during denitrification under anaerobic conditions. Greater production of N_2O instead of N_2 has also been reported during denitrification when NO_3 levels were high (Thomas et al., 1994). Mineral N, such as ammonium and nitrate, can be a regulatory factor in methane oxidation in soils and sediments (Bodelier and Laanbroek, 2004). Börjesson et al. (1998) showed that reduction in CH_4 oxidation was accompanied by an accumulation of NH_4^+ in the soil. In one study (Liikanen and Martikainen, 2003), adding NH_4^+ to eutrophic lake sediment did not affect CH_4 release and CH_4 oxidizing bacteria were not effectively disturbed by the extra NH_4^+. However, Nold et al. (1999) found that NH_4^+ inhibits methane oxidation and production of methanotroph membrane lipids in freshwater sediment. De Visscher and Van Cleemput (2003) showed that NH_4^+ concentration controlled whether CH_4 oxidation was inhibited or stimulated by NH_4^+ in soil. Others have suggested nitrate, rather than nitrite or ammonium, is the strongest inhibitor of CH_4 oxidation in soil (Wang and Ineson, 2003; Reay and Nedwell, 2004). Besides affecting the oxidation of CH_4, $NH_3 + NH_4^+$ was also reported to reduce the production of CH_4 during the anaerobic digestion of food waste (Sung and Liu, 2003).

Increases in S content following PG addition may also affect CH_4 emission since interactions between sulfate-reducing bacteria and methane-producing bacteria have been reported for sediments (Winfrey and Zeikus, 1977; Loveley and Klug, 1983), anaerobic digesters (Isa et al., 1986; Bhattacharya et al., 1996), and peat soil (Blodau and Moore, 2003). Freeman et al. (1994) showed the rate of CH_4 emission decreased with increased sulfate concentration in wetlands. Applying PG to a rice field has

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Abbreviations: EC, electrical conductivity; GHG, greenhouse gas; PG, phosphogypsum; TC, total carbon; TN, total nitrogen; TS, total sulfur.

been reported to decrease CH_4 emissions (Lindau et al., 1998).

The addition of PG to composting livestock manure to conserve N may impact greenhouse gas emissions through effects on compost pH, mineral N content, and sulfate content. The objective of this study was to determine the net effect of PG on GHG emissions during composting of cattle feedlot manure.

MATERIALS AND METHODS

Experimental Design and Setup

The study was conducted in 2002 at the Agriculture and Agri-Food Canada Research Centre, Lethbridge, AB, Canada (49°43′ N, 112°48′ W). Fresh straw-bedded manure (2–6 mo old) from a beef cattle holding pen (with cattle weighing about 220–400 kg) was obtained from the Research Centre feedlot. There were two amendment materials, PG and fine sand. The PG was obtained from a fertilizer plant in Redwater, AB, Canada. The sand was obtained from a local supplier, and was mainly used as an inert filler material to differentiate PG physical bulking effects from its possible chemical and biological effects. The basic properties of manure, PG, and sand are listed in Table 1.

There were six treatments (PG10, PG20, PG30, S10, S20, and S30), representing PG or sand addition at target rates of 10, 20, or 30% of manure dry weight, along with a check treatment with no PG or sand addition. All treatments were replicated three times, giving a total of 21 windrows. The actual rates of addition were 9.9, 20.7, and 30.6% for sand and 10.0, 17.8, and 26.9% for PG treatments. Differences between the target and actual rates were due to variations in moisture content among the materials used in each windrow. The 21 windrows were placed on an earthen pad using a complete randomized design. The basic properties of each treatment at the onset of the experiment are listed in Table 2.

Each windrow covered a base area of about 23 m^2 (3.5 × 6.6 m) with a height of 1.7 m at the beginning of the study. In general, both the base area and the height of the windrow decreased over the course of composting. The windrow was shaped by a front-end loader and the windrow material (manure plus sand or PG) was thoroughly mixed by turning with a tractor-pulled EarthSaver windrow turner (Fuel Harvesters Equipment, Midland, TX). Windrows were turned five times (25 July, 2 August, 22 August, 13 September, and 9 October, corresponding to Days 15, 23, 43, 65, and 91, respectively) after initial construction. The compost experiment ended on 21 Nov. 2002 (Day 134) when the compost windrow temperature dropped below 40°C. At establishment and throughout the composting period, the windrow height, width, length, and circumference were measured at a minimum of three locations to calculate the surface area and volume for each windrow.

Table 1. Properties of cattle manure, phosphogypsum (PG), and sand used in the experiment.

Properties†	Manure	PG	Sand
Water content, g kg^{-1} wet wt. basis	691 ± 8	107 ± 10	64 ± 15
pH‡	8.54 ± 0.03	2.32 ± 0.08	7.83 ± 0.10
Electrical conductivity‡, dS m^{-1}	13.3 ± 0.4	5.8 ± 0.2	0.68 ± 0.02
KCl-extractable NH_4^+–N, mg kg^{-1}	3358 ± 244	642.0 ± 27.5	0.9 ± 0.1
KCl-extractable NO_3^- + NO_2^-–N, mg kg^{-1}	10.6 ± 1.0	1.0 ± 0.3	1.4 ± 0.4
Total N, g kg^{-1}	15.6 ± 0.4	1.6 ± 0.0	0.3 ± 0.0
Total S, g kg^{-1}	4.4 ± 0.1	148.1 ± 11.5	0.7 ± 0.0
Total C, g kg^{-1}	308 ± 10	0.0 ± 0.0	3.8 ± 1.8

† All values are expressed on a dry weight basis unless otherwise indicated.

‡ Obtained using a 1:4 solid to water ratio for manure and PG and 1:0.5 for sand.

Compost Properties

At windrow establishment (8–11 July 2002), before each turning event and the end of the composting (Day 134), samples were taken for manure property determination. Approximately 10 g of fresh manure samples were taken at the windrow peak and at 15, 45, 75, 105, and 130 cm below the windrow peak. Each sample was immediately (on site) put into a 100-mL bottle containing 50 mL of 2 *M* KCl solution. The bottles were then capped and brought back to the laboratory, weighed, shaken for 1 h, and filtered through KCl-washed filter paper (#42; Whatman, Maidstone, UK). The mineral N concentration (NO_2^-, NO_3^-, and NH_4^+) in the extracts was determined by an AutoAnalyzer II (Technicon, Tarrytown, NY).

A separate set of larger (approximately 1 kg) samples were taken at the same locations at the same times. These samples were put into plastic bags and brought back to the lab for analysis. Moisture content was determined gravimetrically by drying in an oven at 60°C. The dried compost materials were initially coarse ground (2-mm) and pH and EC were determined (30 g (dry wt.) of compost with 120 mL of deionized water shaken for 1 h) with a pH/conductivity meter (Accumet pH meter 50; Fisher Scientific, Hampton, NH). Coarse ground subsamples were further ground (0.150 mm) for TC, TN, and TS determination in an automated CNS analyzer (Carlo Erba, Milan, Italy). All results were expressed on a dry weight basis.

Greenhouse Gas Emissions

Gas (O_2, CO_2, CH_4, and N_2O) concentration profiles in each windrow were determined weekly for the first 10 wk and once

Table 2. Characteristics† of initial materials for each treatment.

Treatment‡	Water content	pH§	EC§	NH_4^+–N	NO_3^- + NO_2^-–N	Total N	Total S	Total C	C to N ratio
	g kg^{-1} (wet wt.)		dS m^{-1}	mg kg^{-1}	mg kg^{-1}	g kg^{-1}	g kg^{-1}	g kg^{-1}	
Check	626.3a¶	8.3a	11.7b	2457a	10a	14.0a	4.4c	250.4a	17.9a
PG10	654.6a	7.6b	14.1a	2755a	9a	13.3a	16.2b	236.3a	17.8a
PG20	646.1a	7.6b	15.5a	2311a	6a	13.2a	24.3ab	248.9a	18.9a
PG30	654.6a	7.4b	15.8a	2893a	11a	12.9a	33.9a	238.2a	18.5a
S10	641.2a	8.4a	12.2b	2858a	5a	12.9a	4.1c	259.3a	20.1a
S20	610.7a	8.6a	9.8b	2265a	8a	11.2a	3.8c	191.4a	17.1a
S30	637.3a	8.7a	10.7b	2144a	8a	12.3a	3.6c	231.2a	18.9a

† All values are expressed on a dry weight basis unless otherwise indicated.

‡ Terms represent the rate of phosphogypsum (PG) or sand addition at 10, 20, or 30% of manure dry weight and a check treatment (no PG or sand).

§ Obtained using a 1:4 solid to water ratio. EC, electrical conductivity.

¶ Within a column, values followed by different letters differ significantly at the 0.05 probability level.

every 2 to 3 wk thereafter over the 134-d composting period. Gas samples (10 mL) were collected at 0 (windrow surface), 15, 40, 75, 100, and 130 cm below the surface using a multilevel gas sampler (Hao et al., 2001) with a plastic syringe and injected into 5-mL pre-evacuated vacutainers. All gas samples were taken between 0800 and 1000 h and analyzed for O_2, CO_2, CH_4, and N_2O using a gas chromatograph (Model 3800; Varian Instruments, Walnut Creek, CA) equipped with an electron capture detector (ECD), flame ionization detector (FID), thermal conductivity detector (TCD), and a micro-GC (Varian 4900) equipped with a TCD.

Greenhouse gas surface fluxes during composting were measured on the same schedule as gas concentration profile measurements, using a modified vented chamber technique (Hutchinson and Mosier, 1981). A chamber (15.5 cm in diameter and 15 cm in height) was placed on the peak of the windrow. The 10-mL gas samples were drawn with a plastic syringe from the chamber headspace at 0, 5, 10, 20, and 30 min after chamber placement and immediately injected into 5-mL pre-evacuated vacutainers. All surface flux samples were taken between 0800 and 1000 h and analyzed for CO_2, CH_4, and N_2O as described above.

The concentration versus time relationships for each chamber were fitted with a second-order polynomial equation for each sampling time (SAS Institute, 2001) and the flux at time 0 was calculated by taking derivatives of the second-order polynomials (Hao et al., 2001). Cumulative emissions were approximated by assuming that daily fluxes represented the average for the whole week. To account for emissions during windrow turning, it was assumed that the amount of GHGs released was equivalent to changes in average profile gas concentration before and after turning multiplied by the air-filled pore space in the compost windrow. The gas concentration before turning was measured and concentration after turning was assumed equal to the atmospheric background levels. The emission amounts during turning were added to the total cumulative emissions. The total GHG emissions over the composting period were expressed on an initial unit surface area (kg C m^{-2} or kg N m^{-2} of manure) or initial unit dry weight (kg C Mg^{-1} manure or kg N Mg^{-1} manure) basis.

Weather data were obtained from the Lethbridge Research Centre weather station, <500 m away. Mean daily temperatures were close to normal (11.4–18.9°C) during the 134-d composting period. Total rainfall was 210 mm. More than 50% (110 mm) fell between Days 5 and 40, considerably more than the long-term average of 60 mm. The cumulative pan evaporation was 726 mm for the entire composting period.

Data were analyzed for ANOVA as a one factorial design (with three replications) using Proc GLM in SAS (SAS Institute, 2001). When treatment effects were significant, means among the seven treatments were tested using the Ryan–Einot–Gabriel–Welsch multiple range test. In addition, the relationships between the GHG emission and compost properties were investigated using stepwise linear or nonlinear regression analysis.

RESULTS AND DISCUSSION

Characteristics of Final Compost

The initial mixtures of cattle manure and PG or cattle manure and sand had C to N ratios of 17 to 20 and pH values of 7.4 to 8.7 for all seven treatments (Table 2), within the range for optimal livestock manure composting (Rynk, 1992). Adding PG significantly decreased the pH and increased EC and TS content, but had no significant effect on the water content, mineral N, TN, TC, and C to N ratio of the initial compost mix. Adding sand had no significant effect on any of initial compost mix properties. The lack of differences among treatments was largely due to the inherent large variability in the cattle manure used.

After 134 d, the compost had a pH level of 7.3 to 7.4 for all three levels of PG treatment (Table 3). This was significantly lower than the check (7.8) and sand treatments (7.7–7.9) and was mainly due to the low pH of PG (2.3) (Table 1). The EC values, reflecting the salinity levels, were significantly higher with the PG treatment than the check and sand treatments (Table 3). This is not surprising since PG is primarily gypsum ($CaSO_4{\cdot}2H_2O$), which contributed to the observed high EC in the final compost. However, the increases in EC due to added Ca^{2+} should not be a major concern since most Ca^{2+} would be precipitated as minerals or preferentially adsorbed by soil over K^+ or Na^+ once the compost was applied to agricultural land. Thus, applying high EC compost when Ca^{2+} is the dominant cation should not pose a major problem as would Na^+ or K^+ dominant compost (the main ingredients for soil salinization). In addition, applying a Ca-rich compost may improve soil structure in soils affected by high Na^+ because the addition of Ca^{2+} will decrease the sodium adsorption ratio (SAR).

Mineral N is the sum of KCl-extractable NH_4^+, NO_2^-, and NO_3^-. The NH_4^+ content increased for the first 2 to 3 wk and decreased afterward for all treatments (Fig. 1a). The NH_4^+ content over the course of composting reflects the balance between NH_4^+ production, from

Table 3. Characteristics† of final compost.

Treatment‡	Water content	pH	EC§	NH_4^+–N	NO_3^- + NO_2^-–N	Total N	Total S	Total C	C to N ratio
	g kg^{-1} (wet wt.)		dS m^{-1}	mg kg^{-1}	mg kg^{-1}	g kg^{-1}	g kg^{-1}	g kg^{-1}	
Check	**299.2a¶**	**7.8a**	**10.9b**	**349a**	**488a**	**13.7a**	**5.5d**	**154.5a**	**11.3a**
PG10	**329.0a**	**7.4b**	**15.0a**	**239a**	**580a**	**13.3a**	**16.9c**	**147.5a**	**11.1a**
PG20	**343.0a**	**7.4b**	**16.3a**	**327a**	**683a**	**13.8a**	**28.8b**	**149.8a**	**10.9a**
PG30	**358.9a**	**7.3b**	**15.6a**	**126a**	**579a**	**12.3a**	**34.8a**	**135.0a**	**11.0a**
S10	**304.1a**	**7.9a**	**12.5b**	**213a**	**719a**	**14.2a**	**5.7d**	**158.9a**	**11.2a**
S20	**318.4a**	**7.7a**	**10.7b**	**107a**	**388a**	**12.0a**	**5.4d**	**129.9a**	**10.8a**
S30	**312.3a**	**7.8a**	**11.0b**	**217a**	**519a**	**12.2a**	**5.3d**	**131.4a**	**10.8a**

† All values are expressed on a dry weight basis unless otherwise indicated.

‡ Terms represent the rate of phosphogypsum (PG) or sand addition at 10, 20, or 30% of manure dry weight and a check treatment (no PG or sand).

§ Electrical conductivity.

¶ Within a column, values followed by different letters differ significantly at the 0.05 probability level.

decomposition of organic N, and NH_4^+ loss. This loss occurs through nitrification of NH_4^+ to NO_3^- and volatile NH_3 emissions. The NH_4^+ content in PG-amended treatments was higher throughout the composting period than check or sand treatments with values on Days 62, 89, and 103 being significantly higher. The lower pH values following PG addition would shift the equilibrium between NH_3 and NH_4^+ toward NH_4^+, and therefore a lower NH_3 emission potential. On the other hand, $NO_3^- + NO_2^-$ content remained low for the first 60 d, increased drastically afterward, and reached its maximum on the last day of composting (Fig. 1b). The initial high levels of NH_3 may inhibit the activities of nitrobacter, and therefore NO_3^- only increased after the NH_4^+–NH_3 levels were lowered. After 134 d of composting, the NH_4^+–N content of the compost ranged from 107 to 350 mg kg^{-1} and $NO_2^- + NO_3^-$–N content ranged from 388 to 719 mg kg^{-1} (mainly NO_3^- with NO_2^- contributing $<1\%$). However, no significant differences were found in NH_4^+ or $NO_2^- + NO_3^-$–N content in the final compost product (Table 3) due to large variations among replications.

The TN content of the final compost (12–14 g kg^{-1}; Table 3) was similar to the initial manure mixture (11–14 g kg^{-1}; Table 2). This suggests that N and dry matter were lost at similar rates. The PG and sand treatments had no significant effect on the TN content in the final compost (Table 3).

The TS content of the final compost was significantly higher for the PG treatment than the sand or check treat-

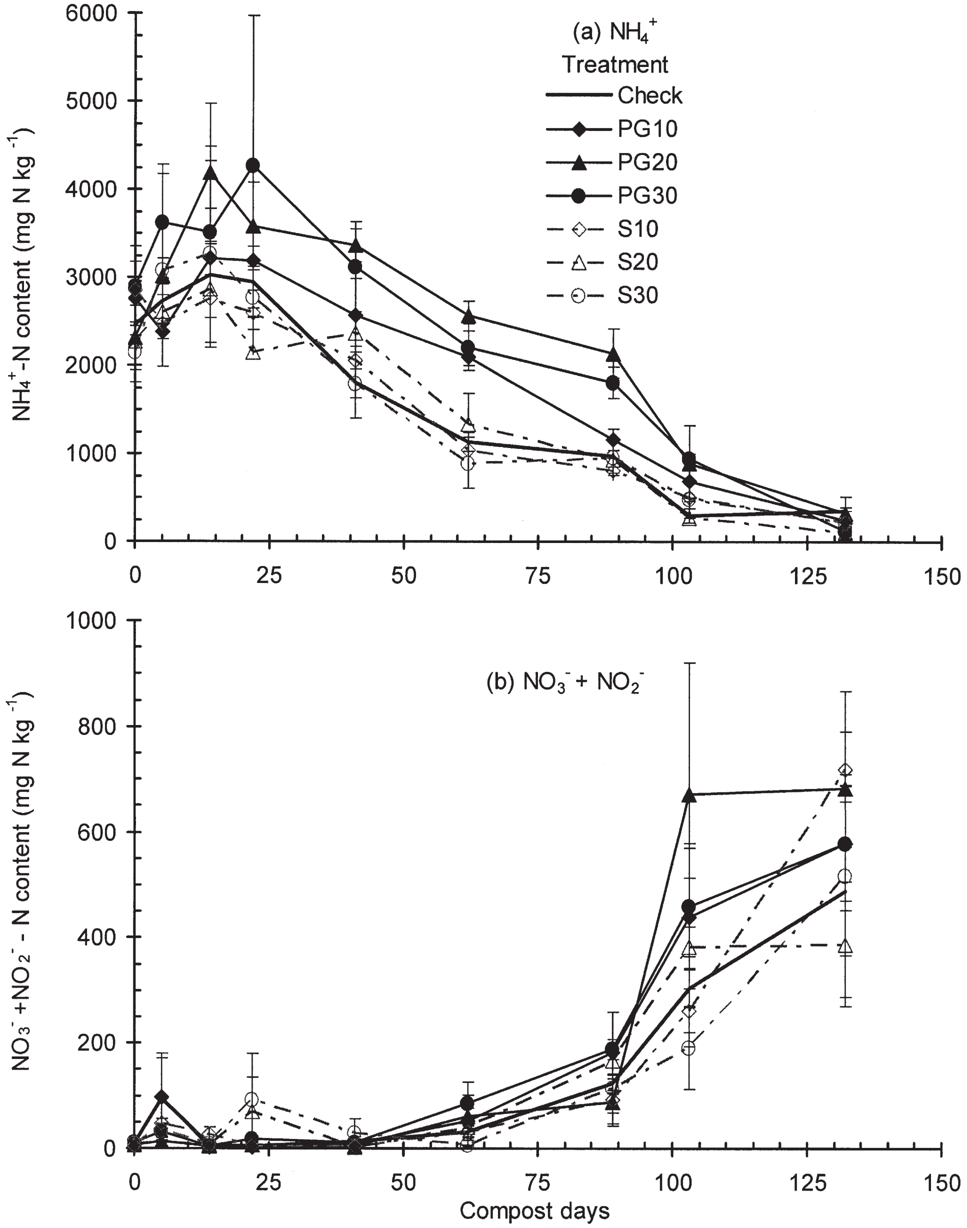

Fig. 1. Change in (a) NH_4^+ and (b) NO_2 + NO_3 concentration during composting as affected by phosphogypsum and sand amendments. Treatment terms represent the rate of phosphogypsum (PG) or sand addition at 10, 20, or 30% of manure dry weight and a check treatment (no PG or sand). The vertical bars are standard errors.

Table 4. Total greenhouse gas (GHG) emission during a 134-d composting.

	Emission rate‡						CO$_2$–C equivalent§			
Treatment†	**CO$_2$–C**	**CH$_4$–C**	**N$_2$O–N**	**CO$_2$–C**	**CH$_4$–C**	**N$_2$O–N**	**CH$_4$–C**	**N$_2$O–N**	**Fuel¶**	**Total**
	kg C m^{-2}		g N m^{-2}	kg C Mg^{-1}		g N Mg^{-1}	kg C Mg^{-1}			
Check	9.82a#	1.610a	1.27a	93.7a	15.36a	12.06a	322.6a	1.60a	3.60	421.5a
PG10	10.54a	0.273ab	2.73a	109.3a	2.83ab	28.29a	59.5ab	3.76a	3.89	176.4a
PG20	10.50a	0.049b	2.06a	109.5a	0.51b	21.50a	10.7b	2.86a	4.12	127.2a
PG30	11.73a	0.039b	2.77a	132.0a	0.44b	30.95a	9.2b	4.11a	4.23	149.6a
S10	11.74a	0.865ab	0.80a	112.4a	8.28ab	7.85a	173.9ab	1.04a	4.10	291.5a
S20	8.95a	1.069ab	1.97a	94.0a	11.23ab	20.83a	235.8ab	2.77a	4.35	336.9a
S30	8.88a	1.176ab	1.30a	100.3a	13.28a	14.66a	278.9a	1.95a	4.71	385.9a

† Terms represent the rate of phosphogypsum (PG) or sand addition at 10, 20, or 30% of manure dry weight and a check treatment (no PG or sand).

‡ Values are expressed per unit initial surface area or dry weight of manure, excluding added PG or sand.

§ Using global warming potential of 1, 21, and 310 for CO$_2$, CH$_4$, and N$_2$O, respectively.

¶ Based on fuel consumption of 0.260 L turn^{-1} Mg^{-1} manure for straw bedding compost turning (B.S. Freeze, personal communication, 2002), and on a CO$_2$–C emission rate of 2.73 kg C L^{-1} diesel fuel.

Within a column, values followed by different letters differ significantly at the 0.05 probability level.

ments (Table 3), reflecting the high S content of PG (Table 2). Total S was initially about 4 to 5 g kg^{-1} in the manure and remained unchanged for check and sand treatments (5–6 g kg^{-1}) in the final compost. Total S content in the final PG treated compost ranged from 17 to 35 g kg^{-1} (Table 3).

During the composting process, CO$_2$ is emitted due to the biological degradation of organic materials. Thus, TC content of the composting materials decreases as composting proceeds. In our experiments, TC levels decreased steadily from initial values of 191 to 259 g kg^{-1} to 130 to 159 g kg^{-1}. The TC content was not affected by sand or PG addition.

Greenhouse Gas Emissions

There were no significant differences among the seven treatments in average daily rate of CO$_2$ emissions, which varied between 65.5 and 87.5 g m^{-2} d^{-1}. The total CO$_2$ emitted during the 134-d composting period varied from 8.9 to 11.7 kg C m^{-2} or 93.7 to 132.0 kg C Mg^{-1} (Table 4). Similar to the TC content, there were no significant differences in the amount of CO$_2$ emitted among all treatments. The C losses through CO$_2$ emission accounted for 33 to 46% of TC initially in the manure. These losses are similar to previously reported values for this region (Hao et al., 2001, 2004). Turning events contributed less than 1% of total CO$_2$ emissions during composting.

Compared with check, rates of CH$_4$ emission were significantly reduced in the PG20 and PG30 treatments, but were unaffected by the addition of sand (Table 4). There was no significant difference between the check and PG10 treatments. The average daily CH$_4$ flux varied from 3.2 to 4.7 g m^{-2} d^{-1} for check and sand treatments, compared with 0.2 to 1.3 g m^{-2} d^{-1} for the PG treatments. The total CH$_4$ emission during the 134 d of composting varied from 0.0865 to 1.610 kg C m^{-2} for check and sand treatments, compared with 0.039 to 0.273 kg C m^{-2} for the PG treatments. Emission of CH$_4$ decreased exponentially with the TS content in the compost (Fig. 2a).

The reduction in CH$_4$ emissions with PG addition could be attributed to several factors. First, PG addition may reduce CH$_4$ emissions by increasing the SO$_4^{2-}$ content of compost. Both sulfate-reducing bacteria and methane-producing bacteria compete for the same organic C and energy sources under anaerobic conditions (Isa et al., 1986; Yoda et al., 1987; Visser et al., 1993; Gupta et al., 1994; Bhattacharya et al., 1996), and sulfate-reducing bacteria may out-compete methane-producing bacteria (Winfrey and Zeikus, 1977; Oremland and Polcin, 1982; Loveley and Klug, 1983). Other studies have shown that the toxic effect of sulfur compounds (SO$_4^{2-}$, S^{2-}, SO$_3^{2-}$–S) on methanogens inhibits CH$_4$ production during anaerobic digestion of industrial wastewater, landfill leachate, and pig house wastewater (Lin et al., 2001; Pender et al., 2004). Methanogenic activity also report-

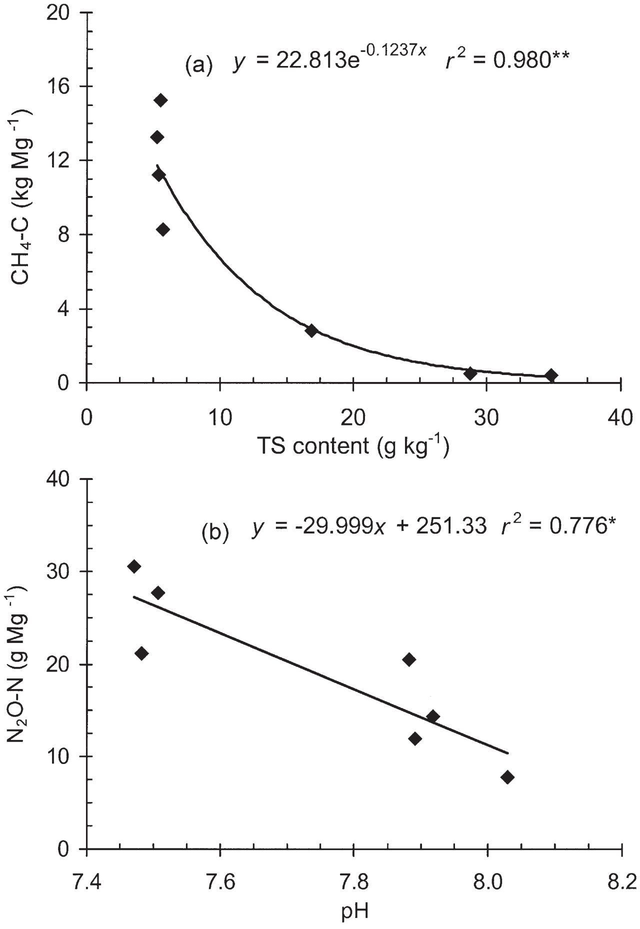

Fig. 2. Relationships between (a) total CH$_4$ emission and total sulfur (TS) content and (b) total N$_2$O emission and pH of the final compost.

edly decreases as the NH_3 + NH_4^+ concentration increases (Sung and Liu, 2003; Sossa et al., 2004). The increases in NH_3 + NH_4^+ content with PG addition (Fig. 1a) could further decrease CH_4 production and contribute to the lower observed CH_4 emission. In addition, the lower pH (Tables 2 and 3) associated with PG treatments could increase the rate of CH_4 oxidation (Hütsch et al., 1994). Although CH_4 oxidation was inhibited by NH_4^+ (De Visscher and Van Cleemput, 2003; Sung and Liu, 2003) or NO_3^- (Wang and Ineson, 2003; Reay and Nedwell, 2004), the higher mineral N content in the PG treatment could potentially increase the CH_4 oxidation rate. The lower CH_4 concentration profiles in the compost windrow and lower surface emission observed when compost mineral N was high under PG treatments suggests the rate of CH_4 production, rather than oxidation, controlled CH_4 emissions during composting.

The amount of CH_4 emitted during composting accounted for 0.2 to 6.1% initial TC and up to 14% of total gaseous C loss (Table 4 and 5). The contribution of CH_4 to total gaseous C loss for the check treatment (Table 5) was higher than previously reported values (Hao et al., 2001, 2004). This is in part due to the higher than normal precipitation (110 mm) during Day 4 to 45 of composting, which increased compost moisture contents and promoted anaerobic conditions and CH_4 production in the compost windrow.

There was no significant difference among the seven treatments in total N_2O emission, which varied between 0.80 and 2.73 g N m^{-2} (Table 4), accounting for 0.06 to 0.20% of initial TN and $<3\%$ of the total N loss (Tables 4 and 5), similar to findings reported from other composting studies (Martins and Dewes, 1992; Kuroda et al., 1996; Eklind and Kirchmann, 2000; Sommer and Møller, 2000; Hao et al., 2001, 2004). However, there was a significant negative relationship between N_2O emission and compost pH (Fig. 2b) based on the average values of the seven treatments. When pH decreased from 8.0 to 7.5 the N_2O emission almost tripled (Fig. 2b), consistent with findings that N_2O emission is generally highest under neutral or slightly acid (pH = 6.5) conditions (Stevens et al., 1998).

In addition to direct GHG emissions, 3.6 to 4.7 kg C Mg^{-1} CO_2 was also released from the diesel fuel burned during composting turning. The amounts released were higher with PG and sand treatments since more material was handled (Table 4).

Using global warming potential factors of 1 for CO_2, 21 for CH_4, and 310 for N_2O, total emissions during composting expressed as CO_2–C equivalents varied from as low as 127.2 to 421.5 kg C Mg^{-1} manure for all treatments. The total GHG emissions with the PG treatments were lower (mainly due to lower CH_4 emission), but the differences were not statistically significant (Table 4). Most C is emitted as CO_2 ($>86\%$ of total C loss), but the impact of CH_4 was greater for the check and sand addition treatments since its global warming potential is 21 times higher than CO_2 (Table 4). Similarly, N_2O contributed less than 3% of the total GHG emission (CO_2–C equivalent), but its emission is of great concern since N_2O is important to troposphere radiation balance and it affects stratospheric ozone chemistry.

There is the potential to mitigate CH_4 emission during livestock composting as demonstrated with PG in this study. Strategies to reduce CH_4 emission may be oriented toward (i) reducing CH_4 production, (ii) increasing CH_4 oxidation, and (iii) reducing CH_4 transport through the compost windrow. This could be achieved through manipulating the aeration, pH, mineral N, and S content in the manure or compost.

Estimation of GHG emission associated with livestock manure handling requires measurement of emission rates under a representative set of environmental conditions. However, identifying the factors that control emission rates is difficult, and there are uncertainties in determining how many different environmental combinations have to be studied to characterize the GHG emitting source. Further studies under controlled laboratory settings are needed to investigate the impact of PG on CH_4 and N_2O emission and determine how different factors, such as pH, mineral N, S, and aeration, interact to develop mitigation technologies.

Mass, Carbon, Nitrogen, and Sulfur Balance

The mass balance for 1 Mg of dry manure was determined for each windrow and the average for each treatment is presented in Table 5. Total dry matter weight increased after PG and sand additions, then decreased

Table 5. Mass, total carbon (TC), total nitrogen (TN), and total sulfur (TS) balance for 1 Mg of manure (dry weight basis).

	Initial					Final					Difference (initial − final)				
Treatment†	M‡	M + A‡	TN	TS	TC	M	M + A	TN	TS	TC	M	M + A	TN	TS	TC
	kg Mg^{-1}														
Check	1000	1000e§	14.0ab	4.4d	250a	793a	780c	11.0a	4.4d	125a	**	**	NS¶	NS	**
PG10	1000	1100d	14.6ab	17.8c	260a	774a	874bc	11.6a	14.0c	129a	*	*	NS	NS	**
PG20	1000	1178c	15.5ab	28.6b	292a	729a	907abc	12.5a	26.1b	136a	**	**	NS	NS	**
PG30	1000	1269b	16.4ab	43.0a	302a	706a	975abc	12.0a	33.9a	132a	**	**	NS	NS	**
S10	1000	1099d	14.2ab	4.5d	285a	762a	861bc	12.5a	4.9d	140a	**	**	NS	NS	**
S20	1000	1207b	13.5b	4.6d	231a	841a	1048ab	12.8a	5.6d	140a	**	**	NS	NS	**
S30	1000	1306a	16.1a	4.7d	302a	795a	1101a	14.0a	5.9d	150a	**	**	NS	NS	**

* Significant at the 0.05 probability level.
** Significant at the 0.01 probability level.
† Terms represent the rate of phosphogypsum (PG) or sand addition at 10, 20, or 30% of manure dry weight and a check treatment (no PG or sand).
‡ M is cattle manure and A refers to PG or sand amendment.
§ Within a column, values followed by different letters differ significantly at the 0.05 probability level.
¶ NS means the differences between initial material and final compost were not significant at the 0.05 probability level.

significantly after 134 d of composting for all treatments (Table 5). The dry matter losses mainly reflect organic matter decomposition and emission of CO_2. Addition of PG or sand increased the amount of finished compost compared with the check treatment (Table 5), thus creating more material to be handled and increasing trucking and field application costs. The total amount of TN and TS decreased during composting, but the differences were not significant (Table 5). Addition of PG or sand did not affect the amount of TN remaining after composting, but TS increased significantly with PG addition, similar to the trend of TS concentration in the initial compost.

Practical Considerations

Canadian livestock production in confined feeding operations faces the continuing challenge of managing manure to remain economically viable and globally competitive. In addition, livestock production must also reduce its environmental impact in the form of greenhouse gas emissions and nutrient loading to surface water. Composting enables livestock manure to be transported greater distances to land where nutrients might be deficient and reduces local nutrient overloading. On the other hand, composting has been shown to emit greenhouse gases, and the use of PG in livestock composting could be an option to reduce CH_4 emissions and the associated global warming effect. The increased S content in compost will also increase its fertilizer value. This would benefit crops that have higher S requirements or soils that are deficient in S. We also need to take into consideration the additional materials to be handled (trucking and field application) if PG were used during composting when developing the best management strategies for livestock manure. The potential for adoption of any technology will depend on economic aspects.

CONCLUSIONS

Composting significantly reduced the amount of C in manure, but the addition of PG or sand did not affect the amount of C lost during composting. For the final compost product, TC, TN, and mineral N were not affected by PG or sand addition. However, the PG treatment significantly increased EC and TS content and decreased pH. For GHG emissions, most C was lost as CO_2 with CH_4 accounting for $<14\%$. Phosphogypsum treatment significantly reduced CH_4 emission, possibly through inhibition or competition effects of S on CH_4 production. There was a exponential decrease in CH_4 emission as compost TS content increased. Emission of N_2O was not significantly affected by PG addition, although it was negatively correlated with compost pH. Further study is needed to examine GHG emissions during composting in response to changes in pH, S, and mineral N content following PG addition to cattle manure. This should be done in a controlled laboratory setting to differentiate the contributions from each factor and reduce the large error terms observed in the field study.

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