

The use of natural materials to control gaseous emissions from decaying organic material

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Management of odorous and polluting gases from wastes is a world-wide challenge. Gaseous losses of nitrogen (N) and sulphur (S) from organic byproducts, such as sewage biosolids, during storage and subsequent land application can be considerable. Laboratory incubation studies were conducted to examine gaseous loss of ammonia (NH₃) and hydrogen sulfide (H₂S) from biosolids under aerobic and anaerobic conditions in order to select an optimum natural medium for odour removal and to help understand the processes involved in odour removal.

The rate of emission of ammonia from the biosolids typically peaked within two days of the experiment and declined rapidly under both aerobic and anaerobic conditions. The total N loss due to NH₃ emission was very low (about 1.87% of total N) and there was no significant difference between the two incubation systems. However, H₂S emissions were higher during anaerobic (7.8% of total S) than aerobic (0.3% of total S) incubation. All natural media tested were found to have an effect on the emission of NH₃ and H₂S, with pine bark and top soil achieving the most efficient reductions. NH₃ emission was reduced by 56% and 46% under anaerobic conditions with the addition of pine bark and top soil, respectively. Addition of pine bark and soil reduced the H₂S emission by 84% and 79%, respectively, under anaerobic conditions. Therefore, the addition of natural materials, such as pine bark and soil, as amendments to biosolids during storage, offers potential for reducing the emission of NH₃ and H₂S.

Introduction

Odours associated with sewage biosolids handling, storage and land application are a major nuisance to the public with complaints about odour emissions being one of the most frequently reported environmental pollution incidents (Goldstein 2001; MfE 2002). Potential adverse health effects from biosolids odours have also been reported (Schiffman *et al.* 2000). Sewage systems are likely to produce emissions of odorous gases, consisting of NH₃, H₂S, volatile organic compounds (VOCs) and "greenhouse" gases including nitrous oxide, carbon dioxide and methane (Luo *et al.* 2004). The most environmentally significant odorous compounds emitted include H₂S and NH₃, because of their high concentrations and/or their low odour thresholds (O'Neill and Phillips 1992).

There are a number of methods available for mitigating odorous emissions from biosolids during processing. These include using biofilters, bioscrubbers and activated carbon (Bowker 1999). Biofilters containing C-rich pine bark have been used successfully to reduce the emission of gaseous N and S compounds from animal rendering facilities and wastewater treatment plants (Luo 2001).

There were two aims of this work: (i) to quantify the gaseous loss of NH_3 and H_2S from stored biosolids held under either aerobic or anaerobic conditions and (ii) to investigate the potential of a range of natural materials to reduce gaseous emissions of NH_3 and H_2S during anaerobic storage of biosolids.

1. Materials and methods

Three sets of experiments were conducted in triplicate to determine the emission of NH_3 and H_2S from biosolids. These included:

- 1) the effect of aeration on gaseous emission from biosolids
- 2) the effect of various amendments on gaseous emission at a single rate of application
- 3) the effect of varying levels of pine bark application on gaseous emission.

De-watered, anaerobically digested biosolids samples (around 10 kg) were collected from wastewater treatment plants in Hamilton and North Shore cities. Around 500g sub-samples were taken and analysed separately before the incubation for their general physical and chemical properties and the results are summarised in Table 1.

After incubation to monitor gaseous emissions, the samples were analysed for total N, S, organic C, mineral N content and pH. Total N was analysed by Kjeldahl digestion followed by titration. The mineral N content (ammonium) was analysed by water extraction followed by colorimetric determination. The total S was measured by hydrochloric/nitric acid digestion and ICP-OES determination. The organic carbon was analysed by combustion and infra-red spectroscopy using a TOC-5000A carbon analyser with a SSM-5000A solid sample module. The pH was measured in water using an Orion Model 370 pH meter fitted with an Orion Model 9202 electrode.

1.1 Experimental design

All incubation experiments were carried out at 20°C using Schott glass bottles with an internal diameter of 70 mm and a capacity of 0.5 litres. The inside of the lid was fitted with a PTFE (Teflon) seal to avoid gas leaks and the side of the bottle was modified to allow connection of two mini-ner[®] valves so that two syringe needles could be introduced; one for the inlet air and the other for exhaust gases.

1.2 Collection and measurement of gases

The gases released from the biosolids in the bottles were passed through two dreschel flasks, the first flask containing 2% boric acid solution to trap NH_3 gas followed by a second containing 0.1M zinc acetate solution to trap H_2S gas. Periodically the traps containing boric acid and zinc acetate solutions were removed and analysed for NH_3 and H_2S , respectively.

The amount of NH_3 absorbed in the boric acid trap was determined by back titration with H_2SO_4 (APHA 1995). The methylene blue colorimetric method was used to determine the amount of H_2S trapped in the zinc acetate solution (APHA 1995). The absorbance of the methylene blue produced was measured using a CE292 spectrophotometer set at 664 nm.

Table 1. Characteristics of biosolids and amendments (wet basis) (Numbers in brackets are standard errors of the mean, n=3).

Property	Biosolid	Amendments			
		Pine bark	Soil	Sawdust	Wood shavings
Total N (%)	1.161 (0.061)	0.23 (0.02)	0.39 (0.02)	0.19 (0.01)	0.19 (0.01)
NH ₄ -N(%)	0.145 (0.009)	53.6 (1.15)	3.87 (0.11)	50.1 (1.21)	48.9 (0.80)
Total P	0.462 (0.113)				
Organic C	4.65 (2.989)				
Total S(%)	0.218 (0.018)				
pH	6.9 (0.144)	4.0 (0.06)	6.5 (0.13)	4.1 (0.19)	4.6 (0.12)
C/N	4.01	233	10	264	257

Experiment 1: The effect of aeration

For each experiment, 100 g biosolids sample was placed in each bottle and incubated under either aerobic or anaerobic conditions. Aerobic conditions were maintained by passing air from a gas cylinder (flow rate was 0.8 dm³/min) into the incubation bottle. Prior to entering the bottle the air was passed through water continually in order to remove any NH₃ and also to maintain the humidity of the sample. Anaerobic conditions were maintained by passing nitrogen gas instead of air through the bottles.

Experiment 2: The effect of addition of a natural material

A range of materials was tested for their ability to remove odorous gases from biosolids under anaerobic conditions. These included wood shavings, sawdust and pine bark (size range of 9-15 mm) from untreated pine timber and obtained from local suppliers. Te Kowhai silt loam soil (Typic Ochraqualf), which is a typical orthic gley, that was passed through a 4-mm screen prior to use, was also included in the experiment. The general characteristics of these materials are summarised in Table 1. Biosolids were mixed thoroughly with each chosen natural material in the proportion of 10 g air dried material to 100 g biosolids. All bottles were incubated under anaerobic conditions.

Experiment 3: The effect of different levels of natural materials

Pine bark only was used to examine the effect of different levels of material addition on gaseous emissions. The bark material was mixed with biosolids as follows: (i) no amendment (control), (ii) 20 g amendment to 100 g biosolids, and (iii) 40 g amendment to 100 g biosolids.

1.3 Data analysis

NH₃ and H₂S losses were calculated based on their measured concentrations in the boric acid solution and zinc acetate solution, respectively, and the mean rates of emission losses were calculated from the three replicates. An analysis of variance was performed using the Genstat statistical package and least significant differences (LSDs) were calculated to estimate the differences between the treatments.

2. Results and discussion

2.1 Aerobic and anaerobic incubations

The average N content of the biosolids was about 1.16% (Table 1). Around 80% of the N content was in an organic form with most of the remainder being $\text{NH}_4^+\text{-N}$. The average C/N ratio was around 4.0. Biosolids pH had increased after 8 weeks of incubation under both conditions (Table 2). Ammonia emission rates reached their peak value within the first two days of the experimental period and declined rapidly, this occurred under both aerobic and anaerobic conditions. This initial high rate of NH_3 volatilisation from the biosolids probably resulted from the large pool of inorganic N available in the biosolids.

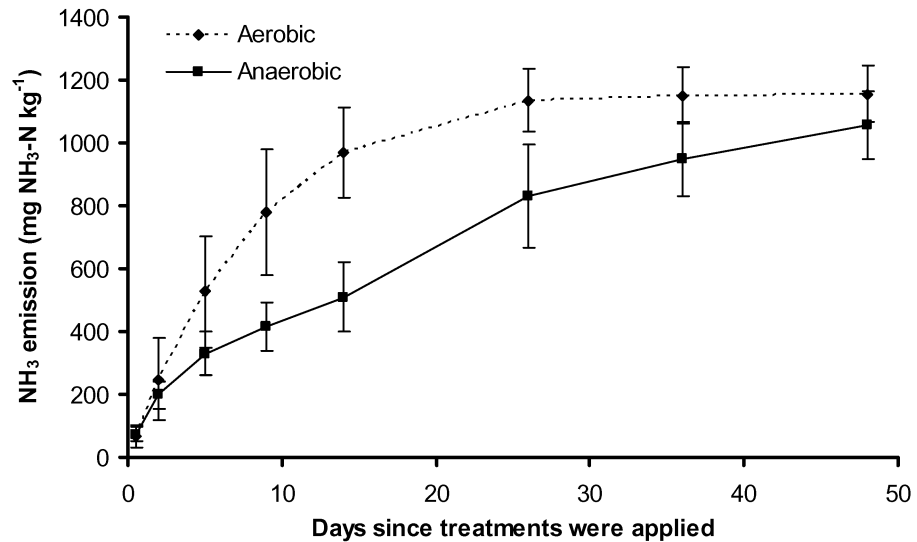


Fig. 1. Cumulative ammonia (NH_3) loss from biosolids in incubation bottles under aerobic vs. anaerobic conditions at 20°C .

Cumulative volatilisation losses of NH_3 from the biosolids during the incubation period are presented in Fig. 1. There was no difference ($P < 0.05$) in the total NH_3 lost between aerobic and anaerobic incubation by the end of the incubation period. Total losses of N from the biosolids, through NH_3 volatilisation during the incubation period, were 1155.8 mg and $1056.6 \text{ mg NH}_3\text{-N kg}^{-1}$ biosolids under aerobic and anaerobic conditions, respectively. The initial biosolids N content was 61.7 g kg^{-1} (Table 2), so these NH_3 volatilisation losses amounted to 1.87% and 1.71% of the initial N content in the biosolids. The biosolids pH increased during the incubation period which may be the reason for the higher rate of NH_3 emission in the aerobic incubation because the rate of NH_3 volatilisation is highly dependant on pH. NH_3/NH_4 ratio increases with pH, thereby increasing the NH_3 volatilisation (Moore *et al.* 1995).

Emissions of H₂S were significantly higher during anaerobic incubation than during aerobic incubation (Fig. 2). The total S loss through H₂S emission was 150.7 mg and 6.1 mg H₂S-S kg⁻¹ biosolids under anaerobic and aerobic conditions, respectively. The initial biosolids S content was 1.92 g kg⁻¹ (Table 2), so these H₂S volatilisation losses amounted to 7.8% and 0.3% of the initial S content of the biosolids. Total S recovery in the biosolids was higher (P<0.05) after aerobic incubation than anaerobic incubation (Table 2).

Table 2. Effects of aeration status on biosolids properties (Numbers in brackets are standard errors of the mean, n=8).

Properties	Before incubation	After incubation	
		Aerobic	Anaerobic
Total N (% in dry basis)	6.17	5.15 (0.138)	5.69 (0.167)
NH ₄ -N (%)	0.13	0.10 (0.014)	0.13 (0.003)
Total S (%)	0.19	0.29 (0.042)	0.21 (0.019)
pH	7.1	8.25 (0.098)	8.89 (0.030)

The rapid release of H₂S from biosolids under anaerobic conditions may have been due to the reduction of sulphates in the presence of a readily available C source, which acted as a reducing agent. As H₂S is highly toxic, precautions are needed to ensure the safety of workers handling stored biosolids. It is likely that H₂S will be emitted at high concentrations when biosolids are taken from anaerobic storage and applied onto fields.

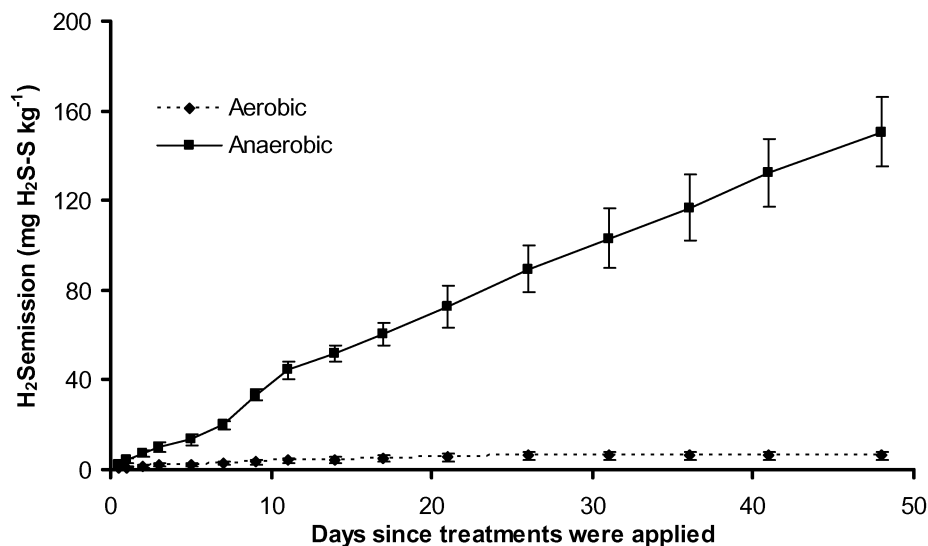


Fig. 2. Cumulative hydrogen sulphide (H₂S) loss from biosolids in incubation bottles under aerobic vs. anaerobic conditions at 20°C.

2.2 Effect of the addition of natural materials on gaseous emissions

The nitrogen content of all the natural materials used was very low and the C content was high in all the materials except soil (Table 1). The pH of the materials was around 4 except for soil, which was around 6.

After six weeks incubation it was found that all the natural materials tested had reduced the cumulative loss of NH_3 due to volatilisation. Pine bark was found to be the most efficient in reducing NH_3 loss, achieving reduction of 56% compared with unamended biosolids (Table 3), followed by soil (46%), wood shavings (41.5%) and sawdust (36%). There were no significant ($P < 0.05$) differences in NH_3 volatilization amongst the treatments of soil, sawdust and wood shavings. The reduction in NH_3 volatilisation from biosolids due to addition of pine bark was significant ($P < 0.05$) with both the ratios tested (Table 4).

The driving force for the volatilisation of NH_3 from biosolids is the difference in partial pressure of NH_3 between the liquid phase and atmosphere. The partial pressure of NH_3 in the liquid phase is controlled by the pH and the NH_4^+ ion concentration (Lauer *et al.* 1976). Lowering the pH of the biosolids or decreasing the amount of NH_4^+ ions present will reduce the volatilisation of NH_3 . The beneficial effect of organic-rich amendment materials in reducing NH_3 volatilization is attributed to direct absorption of NH_4^+ ions and NH_3 (Witter and Kirchmann 1989) and/or enhanced microbial N immobilization (Kirchmann and Witter 1989). In this study, lower amounts of NH_4^+ ions were measured in the bark amended biosolids compared to the unamended biosolids after incubation (Table 5). Hence, the reduction in NH_3 loss was probably caused by the immobilization of NH_4^+ ions by the woody materials. Net immobilization of N occurs when the C:N ratio is ≥ 15 (Castellanos and Pratt 1981), so immobilization would be expected in this experiment where the initial C/N ratios of all the treatments, except soil, were higher than 15. Increasing the proportion of pine bark addition to the biosolids resulted in a higher C/N ratio, thereby increasing N immobilization. This could be one of the reasons for the further decrease in NH_3 volatilisation.

The pH of the biosolids was consistently above 7 and the addition of natural materials decreased the pH slightly. Reductions in pH may be one of the factors causing lower NH_3 volatilisation in the amended biosolids than in the unamended biosolids. Pine bark has a large total surface area and cation exchange capacity and NH_4^+ ions and organic N compounds can adsorb onto surfaces, as demonstrated by the fact that the sorption of odorous compounds was one of the important mechanisms in removal of odours by biofilters using pine bark media (Luo and van Oostrom 1997). However, the physical, chemical and biological processes occurring in a biofilter medium are complex and accurate information is not available. Factors affecting removal of NH_3 in a biofilter include nutrient content, water holding capacity, pH, structure and surface texture (Devanny *et al.*, 1999). The reduction in NH_3 volatilization resulting from the addition of soil to the biosolids is likely to have been due to the soil's exchange capacity for NH_4^+ ions.

At the end of 6 weeks incubation the cumulative H_2S emission losses were significantly ($P < 0.05$) reduced by the addition of natural materials (Table 3): pine bark reduced the H_2S emission by 83%, followed by soil (79%), wood shavings (71.2%) and sawdust (57%). Increasing the proportion of pine bark addition to the biosolids from 2% to 4% did not significantly ($P < 0.05$) increase the efficiency in reduction of H_2S volatilisation (Table 4). Cumulative H_2S emissions were reduced by 72% and 76% with 2% and 4% bark addition, respectively.

As these experiments were conducted under controlled laboratory conditions, appropriate care should be taken when extrapolating the results to full-scale biosolids storage systems. The technological aspects of the use of natural materials to manage biosolids N and S dynamics at an operational scale have not been addressed in this study.

Table 3. Effect of natural amendments (10g amendment/100g biosolids) on cumulative amount of ammonia (NH₃) and hydrogen sulphide (H₂S) loss from biosolids during anaerobic incubation (mgkg⁻¹ biosolids).

	NH ₃		H ₂ S	
	emission	% reduction	emission	% reduction
Control	698.61		124.49	
Pine bark	305.36	56.29.	20.5	83.53
Top soil	376.13	46.16	25.43	79.57
Wood shavings	408.4	41.54	35.83	71.22
Saw dust	449.16	35.71.	52.72	57.65

Table 4. Effect of varying level of pine bark on cumulative amount of ammonia (NH₃) and hydrogen sulphide (H₂S) loss from biosolids during anaerobic incubation (mgkg⁻¹ biosolids).

	NH ₃		H ₂ S	
	emission	% reduction	emission	% reduction
Control	680		116	
Pine bark 20g/100g biosolids	339	50.2 %	32	72.2 %
Pine bark 40g/100g biosolids	288	57.7 %	27	76.3 %

Table 5. Effects of pine bark amendment on biosolids properties (Numbers in brackets are standard errors of the mean, n=3).

Properties	Before incubation	After incubation		
		Treatment		
	Control	Control	20 g bark	40 g bark
Total N (%)	1.13	1.087 (0.066)	0.959 (0.044)	0.870 (0.030)
Organic N (%)	nd	0.886	0.866	0.805
NH ₄ ⁺ -N (%)	nd	0.201 (0.026)	0.093 (0.018)	0.065 (0.014)
Total S (%)	0.21	0.221 (0.005)	0.191 (0.008)	0.184 (0.015)
pH	7.1	8.2 (0.10)	7.1 (0.15)	6.7 (0.03)

*nd = no data

3. Conclusion

The initial high rate of NH₃ volatilisation from stored biosolids probably resulted from the high inorganic N present, because organic N needs to be mineralized before it becomes volatile. In the later stages, NH₃ can be volatilised as a result of biological processes mineralizing the organic N. The rapid release of H₂S from biosolids under anaerobic conditions may have been due to the reduction of sulphates in the presence of readily available C sources which acted as reducing agents.

Addition of natural materials to biosolids can be an effective means of conserving the N and S in the biosolids, thereby reducing emissions. Amongst the four natural materials examined, pine bark was found to be the most effective in reducing losses of both NH₃ and H₂S, but the other test substrates also had a significant effect. The reduction was probably caused by immobilization of mineral N and S and adsorption of N and S compounds by the natural materials.

4. References

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