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Title:
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Date:
2015-01-01

Citation:
Majumder, R., Livesley, S. J., Gregory, D. & Arndt, S. K. (2015). Storage management influences greenhouse gas emissions from biosolids. Journal of Environmental Management, 151, pp.361-368. https://doi.org/10.1016/j.jenvman.2015.01.007.

Persistent Link:
https://hdl.handle.net/11343/58812

Storage management influences greenhouse gas emissions from biosolids

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Abstract

Biosolids produced by wastewater treatment plants are often stored in stockpiles and can be a significant source of greenhouse gases (GHG). Growing trees in shallow stockpiled biosolids may remove nutrients, keep the biosolids drier and offset GHG emissions through C sequestration. We directly measured methane (CH_4), carbon dioxide (CO_2) and nitrous oxide (N_2O) flux from a large biosolid stockpile and two shallow stockpiles, one planted with *Salix reichardtii* (willow) trees, from December 2009 to January 2011. All stockpiles emitted large annual amounts of GHG ranging from 38 kg CO_2-e Mg^{-1} dry biosolid for the large stockpile, to 65 kg CO_2-e Mg^{-1} for the unplanted shallow stockpile, probably due to the greater surface area to volume ratio. GHG emissions were dominated by N_2O and CO_2 whilst CH_4 emissions were negligible (< 2%) from the large stockpile and the shallow stockpiles were actually a CH_4 sink. Annual willow tree growth was 12 Mg dry biomass ha^{-1}, but this only offset 8% of the GHG emissions from the shallow planted stockpile. Our data highlight that biosolid stockpiles are significant sources for GHG emissions but alternate management options such as shallow stockpiles or planting for biomass production will not lead to GHG emission reductions.

Keywords: Sewage sludge, respiration, biomass, carbon offset, sequestration, nitrous oxide, methane.

1. Introduction

Biosolids are an end product of the sewage treatment processes and their production gradually increases every year due to sewage production from an increasing human population (Wang et al., 2008). For example, in Australia there is an approximate 3% increase in biosolid production from wastewater treatment plants (WTPs) annually (AWA, 2013). The storage of biosolids within WTPs is necessary either temporarily, or long-term, depending upon whether an ultimate end-use is available. Desirable end uses have a low environmental impact or even an environmental and economic benefit, such as biosolid application to agricultural or production forestry systems (Pritchard et al., 2010). Biosolids are often stored in large stockpiles to minimize the use of space, but this can present a fire risk (spontaneous combustion), pollution risks (leachate and particulate) and increased GHG emission risks as they are rich in organic matter and nutrients (Fernandes et al., 2005). In fact, biosolid stockpiles can emit large amounts of greenhouse gases, especially in young stockpiles (Majumder et al., 2014).

A potential alternative end use, or long term storage option for biosolids are shallow stockpiles (e.g. 0.5 m deep) over larger areas and within which woody vegetation can be planted for carbon offset gains, biosolid stabilization and pollutant/nutrient removal (Laidlaw et al., 2012). In such a system, the high labile carbon and nitrogen content of the biosolid, in combination with rainfall and/or supplementary irrigation, could lead to high plant biomass production and therefore a value adding product for bioenergy or biochar production and/or carbon offset potential of related GHG emissions from the WTP. However, microbial decomposition and transformations of labile carbon and nitrogen in these stockpiles may still lead to significant production of methane (CH_4), carbon dioxide (CO_2) and nitrous oxide (N_2O) under aerobic and anaerobic conditions. In WTPs, GHG emissions are generally estimated using emission factors based on the initial chemical properties of the wastewater or sewage sludge (Brown et al., 2010) and as such there is substantial uncertainty in these GHG emissions estimates (Bogner et al., 2008). This also relates to the storage and management of dried biosolids as direct measurements of GHG emissions from biosolids in stockpiles or other interim storage options are lacking.

The main aim of this study was to assess the magnitude of GHG emissions from three different biosolid storage and management systems: i) large stockpiles (LS), ii) unplanted shallow stockpiles (USS) and iii) planted shallow stockpiles (PSS) with willow (*Salix x reichardtii* A.Kern).

The specific objectives of this study were to:

(1) measure the seasonal variation and magnitude of CH_4, CO_2, and N_2O emissions from the three different biosolid management options;

(2) investigate the relationship between greenhouse gas fluxes and environmental variables in these storage management systems;

(3) calculate the annual CH_4, CO_2, and N_2O flux balance from the three different biosolid management systems and evaluate the carbon offset potential of woody biomass growth in biosolids.

2. Materials and method

2.1 Experimental set-up and site description

The study site was located at the Western Treatment Plant (WTP) of Melbourne Water, which is located in Weribbee, 35 km south-west of Melbourne (37°59’35’’S, 144°36’58’’E). The WTP treats wastewater of around 1.8 M people of the western and northern suburbs of Melbourne. The temperate climate in the region is characterized by warm and dry summers and a relative even rainfall distribution with a maximum in spring. Historical average annual rainfall (1941-2012) is 514.4 mm (BOM, 2013). Currently, there are approximately 1,573,000 Mg of air-dried biosolids stockpiled at the WTP (MelbourneWater, 2010). For this study, three different management practices of biosolids storage and use were selected to quantify their GHG emissions. These were: i) large stockpiles (LS), which are commonly used (~9.0 m high), ii) unplanted shallow stockpiles (USS = 0.5 m high) and iii) planted shallow stockpiles (PSS = 0.5 m high) with willow (*Salix x reichardtii* A.Kern). The same biosolids were used for all three management options. The biosolids were collected before 1995 from the mixed sludge of a number of drying pans and were stored in biosolid stockpiles prior to the experiment commencing. The experimental area of shallow stockpiles was set up in 2005 and covered an area of approximately 7000 m^2, with 2000 m^2 of this being planted with willows at a stocking rate of 40,000 plants ha^{-1} (or 4 plants m^{-2}). The willow planting was irrigated with Class C waste water during the summer months, see Laidlaw et al. (2012) for more details.

2.2 Measurement of GHG flux from three different management practices of biosolid

The GHG flux rates of CH_4, CO_2 and N_2O were measured using the closed static chamber technique (Hutchinson and Mosier, 1981) at the surface of each stockpile in the management practices LS, USS and PSS. We collected gas samples once a month from December 2009 to January 2011. On the top of each stockpile we placed eight chambers in a row about 1-2 m apart. The manual chambers consisted of non-transparent PVC pipe (diameter 25 cm, height 24.5 cm, volume 12.0 L) and had a twist-lid incorporating a butyl-rubber septum and a rubber O-ring to form a gas tight seal. The basal area of each chamber was 0.045m^2. Manual chambers were inserted to a depth of 3-4 cm depth at least 15 to 30 minutes before closing the lid. After closing the chamber lids, we collected 20 mL headspace gas samples with a syringe at intervals of 0, 4, 8 and 12 minutes for the large stockpile and at intervals of 0, 10, 20 and 30 minutes for the shallow stockpile because of initial differences from trial gas flux measures. The gas samples were collected between 10:30 and 14:30 in pre-evacuated 12 mL vials (Exetainers™, Labco Pty Ltd, UK). After collecting gas samples, chamber height was measured at four positions to calculate head space volume of each chamber individually. Gas samples were analyzed using gas chromatography (GC) (Shimadzu GC17A, with N_2 carrier gas) to determine CH_4 concentrations using a flame ionization detector (FID) and CO_2 concentrations through the addition of a Methaniser (SRI Instruments, USA) before the FID. N_2O concentrations were determined using an electron capture detector (ECD) in the same GC run.

2.3 Measurement of biosolid environmental properties

We measured biosolid temperature (BT) with short temperature probes (Cole-Parmer, USA) at a depth of 10 cm at the same time as gas samples were collected. We collected biosolid samples at each measurement from the upper 0.1 m with a stainless steel bulk density ring near each chamber to estimate biosolid moisture content (MC), bulk density and to provide samples for NO_3^- and NH_4^+ concentration analysis. We dried subsamples at 105°C for 48 hours and determined biosolid MC gravimetrically by weighing samples before and after drying. The NO_3^- and NH_4^+ concentration of biosolids was measured in 1 M KCl extracts (1:4, biosolid:KCl) on a Technicon^{TM} auto-analyser. The bulk density of biosolids was calculated dividing the mass of oven dried biosolids (g) by the volume of stainless steel ring (cm^3) (Gifford and Roderick, 2003).

2.4 GHG flux calculation

Curvilinear regressions best described the CH_4, CO_2 and N_2O fluxes from biosolid stockpile because the gas concentration in the chamber headspace decreased gradually with time of chamber closure (Matson and Harriss, 1995). The following equation was used to measure the flux

$$f_o = V * (C_1 - C_0)^2 / [A * t_1 * (2 * C_1 - C_2 - C_0)] * \ln [(C_1 - C_0)/(C_2 - C_1)] \qquad (1)$$

where, f_o is the flux at time 0, V is the chamber headspace volume (L), A is the soil surface area (m^2), C_0, C_1, and C_2 are the chamber headspace gas concentrations ppm(v) at different times after closure (0, 4, 8 and 12 minutes for LS and 0, 10, 20, 30 minutes for USS and PSS), respectively, and t_1 is the time between gas sampling points (Minato et al., 2013). The unit of f_o is µL trace gas m^{-2} min^{-1}.

This flux (f_o) was then transformed to µmol CH_4, CO_2 and N_2O m^{-2} h^{-1} by accounting for pressure, temperature and volume based on the ideal gas law by applying Equation 2

$$F_{\mu mol} = \frac{F_{\mu L} \times P}{R \times T} \qquad (2)$$

where $F_{\mu mol}$ is the flux in µmol CH_4, CO_2 and N_2O m^{-2} h^{-1}, $F_{\mu L}$ is the flux in µL CH_4, CO_2 and N_2O m^{-2} h^{-1} , P is the atmospheric pressure in kPa at the site depending on the altitude, T is air temperature in K (273 + ºC), R is the ideal gas constant = 8.3144 L kPa mol^{-1} K^{-1}). The fluxes of µmol CH_4, CO_2 and N_2O m^{-2} h^{-1} were converted to µg CH_4-C, CO_2-C and N_2O-N m^{-2} h^{-1} depending on the molecular mass of each gas.

We measured fluxes prior to the start of the campaigns at different times of the day and we observed only small diurnal variation of flux for all GHG. We therefore decided to measure the GHG always in the same time window (see above) and estimated the daily flux of CH_4, CO_2 and

N_2O, by multiplying the hourly flux (μg kg^{-1} hr^{-1}) of each measurement day by 24 hrs. The monthly flux of CH_4, CO_2 and N_2O, was calculated by multiplying the mean daily flux (μg kg^{-1} d^{-1}) by the days of each month. To compare the global warming potential of the different gases we converted the monthly flux to kg CO_2-e m^2 $month^{-1}$ for CH_4 and N_2O flux by using a global warming potential of 25 for CH_4 and 298 for N_2O (IPCC, 2007). Monthly kg CO_2-e Mg^{-1} dry biosolid was estimated based on m^2 monthly flux of CH_4, CO_2 and N_2O of each stockpile and total dried biosolid mass (using total area, bulk density, total volume of each stockpile and moisture content).

2.5 Carbon sequestration in woody biomass

Woody biomass was harvested from a short rotation coppice of willow planted on 2,000 m^2 of the shallow (0.5m) biosolid stockpile. This willow rotation coppice consisted of 40,000 cuttings per hectare (4 plants m^2) that were harvested/coppiced once every year. After three years of annual rotation the average above-ground woody biomass production (oven dry basis) was approximately 12 Mg ha^{-1} (Laidlaw et al., 2012). It was estimated that one dry Mg of 0.5 m high biosolid stockpiled could cover 2.0243 m^2. As such, one dry Mg of biosolid could support the growth of 2.4 kg of dry woody biomass (above ground). Carbon sequestration was estimated under the assumption that 50% of dry woody biomass is carbon (Zhang et al., 2012).

2.6 Data analysis and presentation

Sigma Plot 12.0 and Excel 2007 were used to analyze the data. We evaluated the significance of relationship between CH_4, CO_2 and N_2O flux and moisture content, biosolid temperature, NO_3^--content and NH_4^+-content using simple linear regressions. We calculated the total annual emissions (kg Mg^{-1}dry biosolids) of CH_4, CO_2 and N_2O (CO_2-e) by dividing the total GHG emissions (kg Mg^{-1}dry biosolids) from measured months by the number of measured months and multiplying it by 12.

3. Results

3.1 Seasonal variation in GHG emissions from biosolid storage management systems

Of the three different biosolid storage management systems, the LS treatment had the lowest average monthly N_2O emissions (1.0 kg CO_2 e Mg^{-1} dry biosolid) and the highest average monthly CH_4 emissions (0.054 kg CO_2 e Mg^{-1} dry biosolid). The LS was a continuous source of CH_4, with greatest emissions in September and November 2010 **(Figure 1)**. Monthly N_2O emissions from LS ranged between 0.14 and 4.4 kg CO_2-e Mg^{-1} dry biosolid and peaked in January and November 2010. The CO_2 emissions fluctuated but gradually decreased from 4.1 kg to 2.3 kg CO_2 e Mg^{-1} dry biosolid by the end of this study period.

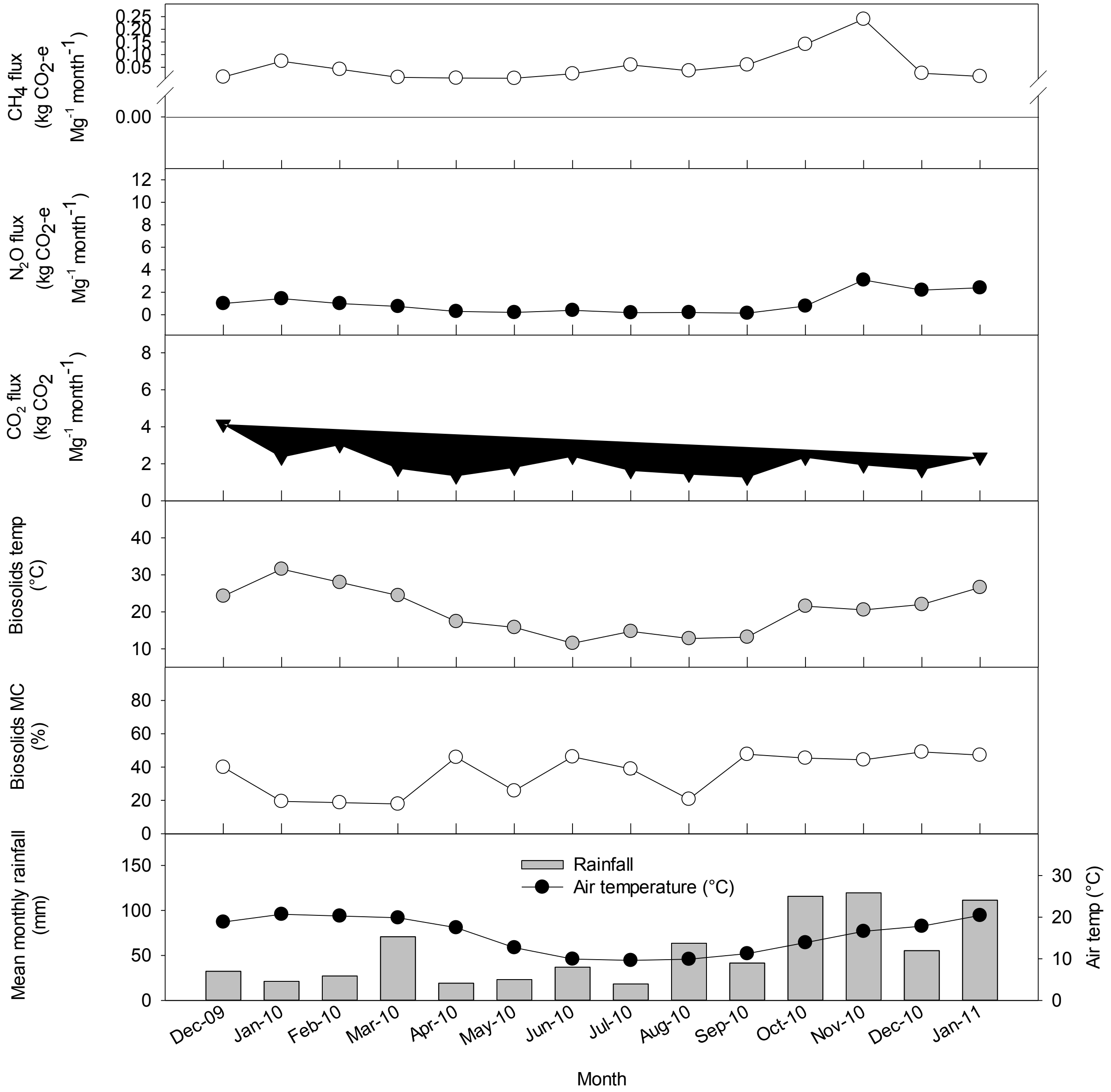

Figure 1. Fluxes of CH$_4$, N$_2$O and CO$_2$ (kg CO$_2$-e Mg biosolid^{-1} month^{-1}) from a large stockpile (LS) (n=8) at the Western Treatment Plant in Melbourne, Australia.

In the USS treatment, we measured zero to slightly negative CH$_4$ flux indicating the presence of methane uptake by the biosolids and overall the stockpile was a small CH$_4$ sink **(Figure 2)**.

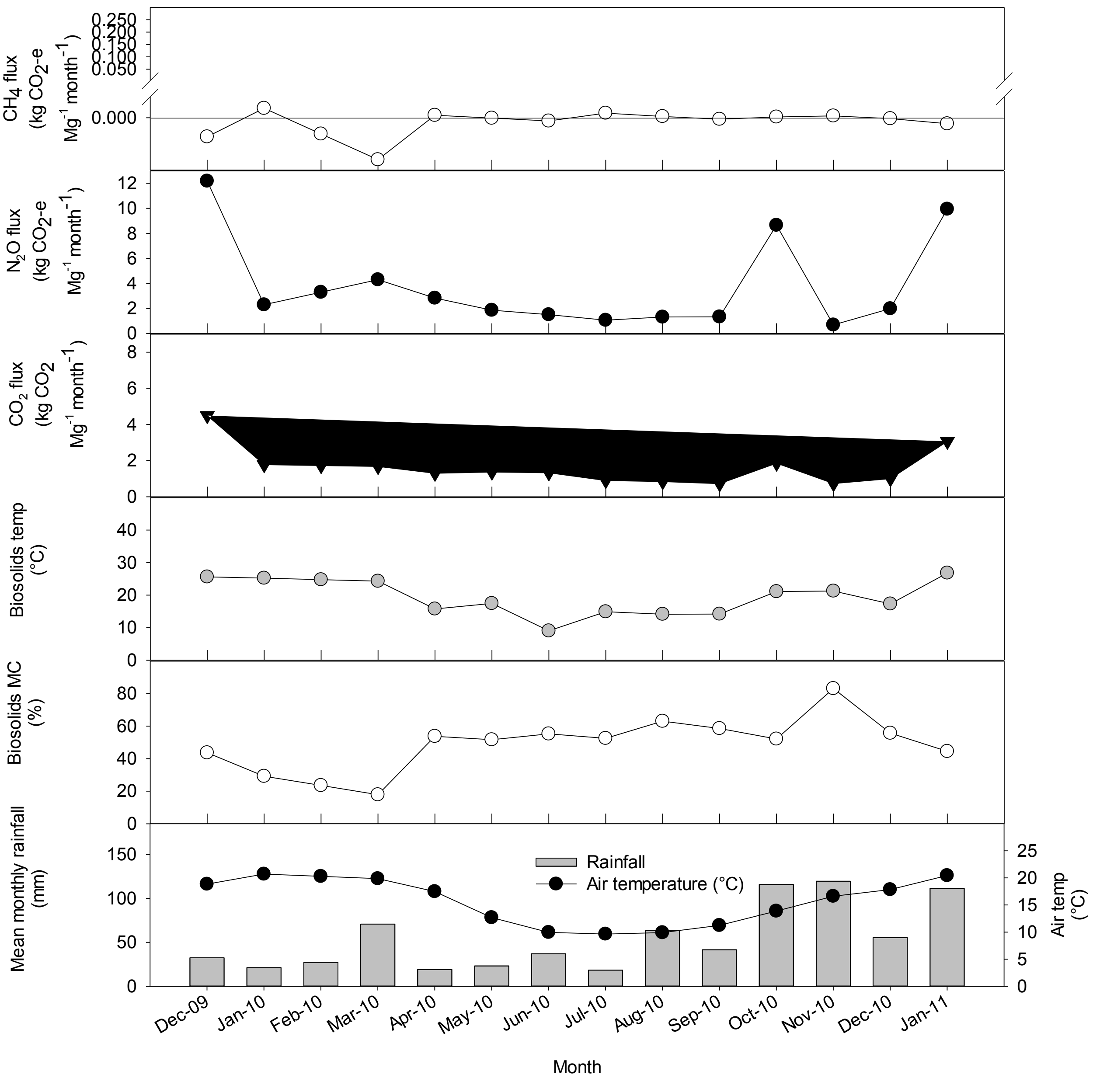

Figure 2. Fluxes of CH$_4$, N$_2$O and CO$_2$ (kg CO$_2$-e Mg biosolid^{-1} month^{-1}) from an unplanted shallow stockpile (USS) (n=8) at the Western Treatment Plant in Melbourne, Australia.

The monthly measured CO$_2$ emissions were between 0.72 and 4.5 kg CO$_2$ e Mg^{-1} dry biosolid. The highest emissions of CO$_2$ were observed at beginning and end of the study, in summer months. N$_2$O emissions from USS ranged between 0.7 and 12.1 kg CO$_2$ e Mg^{-1} dry biosolids month^{-1} and were greatest in December 2009, October 2010 and January 2011, spring and summer months.

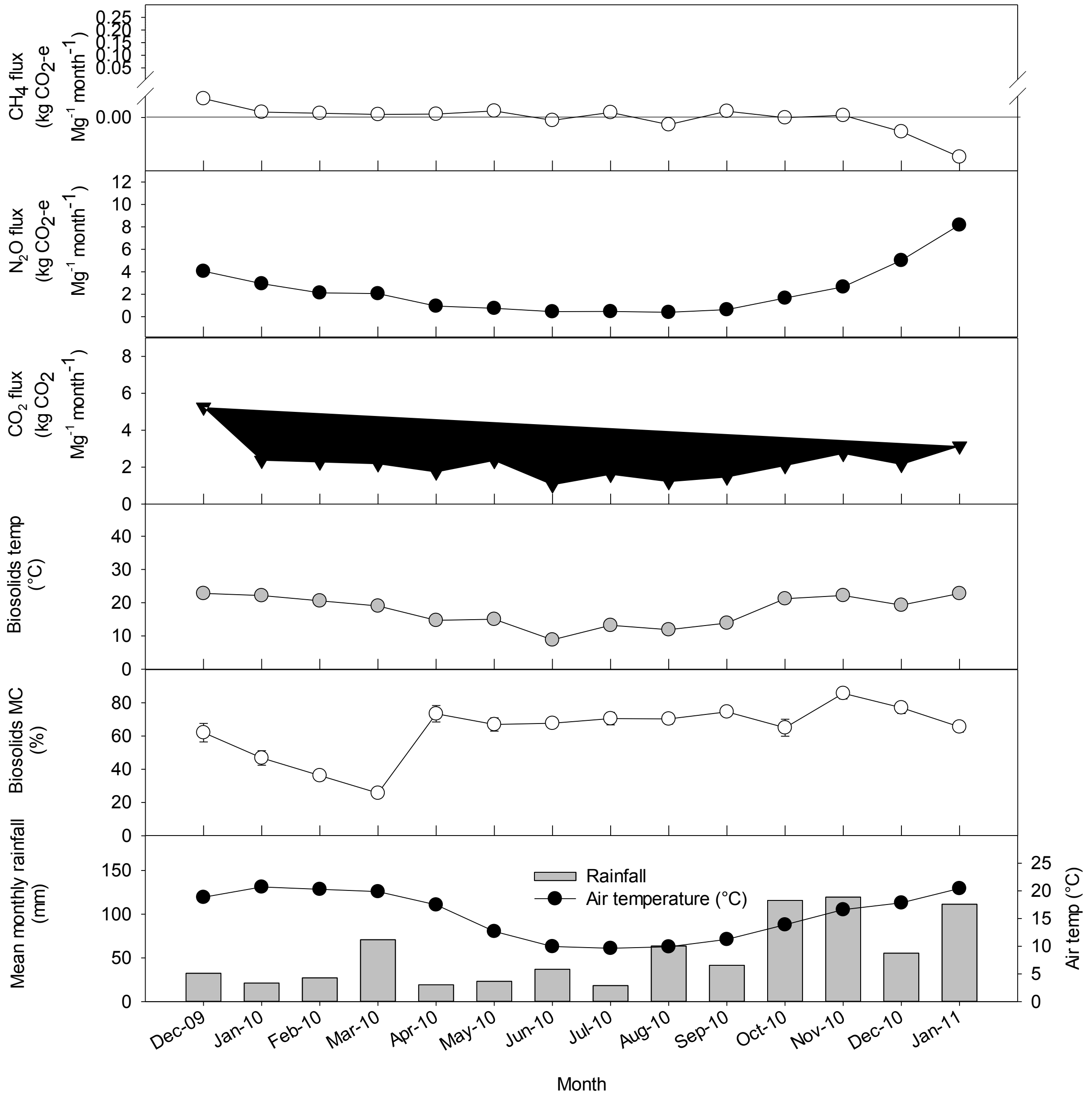

Figure 3. Fluxes of CH_4, N_2O and CO_2 (kg CO_2-e Mg biosolid^{-1} month^{-1}) from a planted shallow stockpile (PSS) (n=8) at the Western Treatment Plant in Melbourne, Australia.

The PSS treatment also had zero to slightly negative CH_4 flux indicating the presence of methane uptake by the biosolids and was a small CH_4 sink (Figure 3). Monthly measured CO_2 emissions from PSS were slightly greater than from USS, ranging between 1.0 and 5.25 kg CO_2 e Mg^{-1} dry biosolid. In PSS the monthly measured N_2O emissions were between 0.4 and 8.1 kg CO_2 e Mg^{-1} dry biosolid and were greatest in December and January of both measured summers.

3.2 Seasonal variation in biosolid environmental properties

The average moisture content of PSS and USS were between 49-63% and the average moisture content was higher in PSS as compared to USS (Figures 1, 2 and 3). The average moisture content was very low (36%) in LS. We observed the greatest moisture content in all three stockpiles in the months of October 2010, November 2010 and January 2011 due to heavy rainfall. The average monthly rainfall of those three months was 115 mm. The average biosolid temperature was greater in LS (20°C) as compared with PSS (18°C) and USS (19°C). The highest biosolid temperature was observed in December 2009 to February 2010.

The average NO_3^--N content was greatest in the LS (190 mg N kg^{-1}), more than twice than in USS (72 mg N kg^{-1}) and three times greater than in PSS (53 mg N kg^{-1}) (Figure 4). We observed less disparity and variation in the average NH_4^+-N contents, which were greater in USS (9 mg N kg^{-1}) than PSS (5 mg N kg^{-1}) and the LS (1 mg N kg^{-1}).

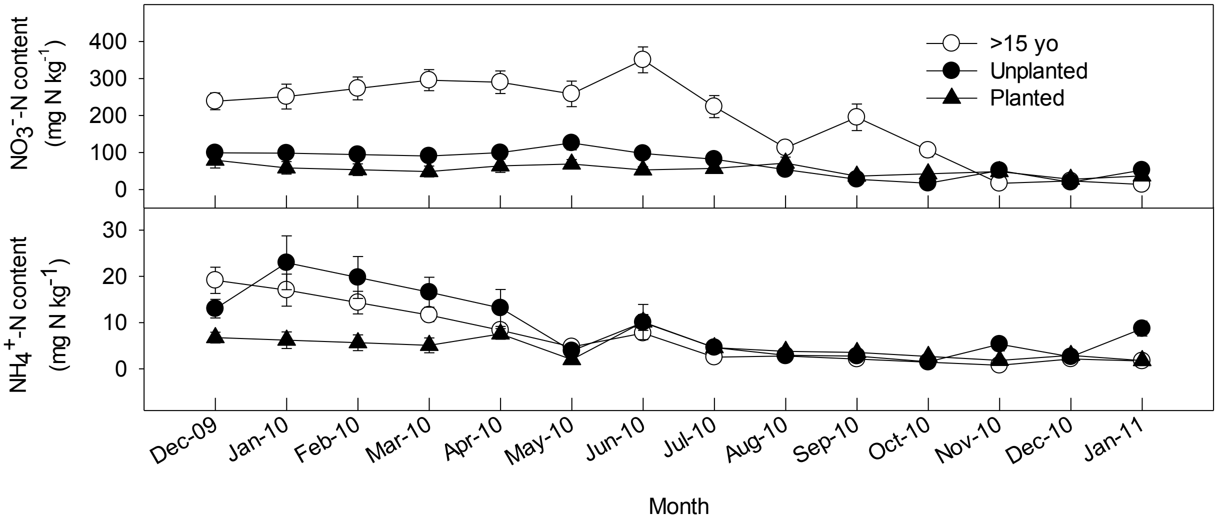

Figure 4. Monthly NO_3^- and NH_4^+ concentration (mg N kg^{-1}) from the large stockpile (LS), unplanted shallow stockpile (USS) and planted shallow stockpile (PSS) (SE, n=8) at the Western Treatment Plant in Melbourne, Australia.

3.3 Relationships between biosolid environmental variables and GHG flux

We observed only weak relationships between MC and GHG flux in all biosolid stockpile treatments. A significant ($p \leq 0.05$) but weak correlation existed between MC and CH_4 flux for USS **(Table 1)**. But we did not detect any significant relationship between MC and CH_4 flux in the LS or PSS treatments. We also did not observe any significant relationship between MC and either N_2O or CO_2 emissions from either of the three treatments.

Table 1. The relationship and level of significance between fluxes of methane (CH_4), nitrous oxide (N_2O) and carbon dioxide (CO_2) and biosolid moisture content (MC), biosolid temperature (BT), NO_3^--N concentration and NH_4^+-N concentration at 10 cm depth in large stockpile (LS), unplanted shallow stockpile (USS) and planted shallow stockpile (PSS) management system at the Western Treatment Plant in Melbourne, Australia.

	GHG flux (kg CO_2-e dry Mg biosolid^{-1} month^{-1})					
Stockpiles	CH_4		N_2O		CO_2	
MC at 10 cm (%)	R^2	*p*	R^2	*p*	R^2	*p*
LS	0.04	ns	0.05	ns	0.07	ns
USS	0.36	<0.05	0.09	ns	0.09	ns
PSS	0.02	ns	0.007	ns	0.01	ns
BT at 10 cm (°C)						
LS	0.003	ns	0.31	<0.05	0.47	<0.05
USS	0.17	ns	0.38	<0.05	0.41	<0.05
PSS	0.01	ns	0.38	<0.05	0.53	<0.05
NO_3^--N concentration (mg N kg^{1})						
LS	0.23	ns	0.49	<0.05	0.04	ns
USS	0.05	ns	0.004	ns	0.06	ns
PSS	0.32	<0.05	0.14	ns	0.18	ns
NH_4^+-N concentration (mg N kg^{-1})						
LS	0.12	ns	0.02	ns	0.61	<0.05
USS	0.14	ns	0.02	ns	0.13	ns
PSS	0.15	ns	0.11	ns	0.24	ns

We observed only weak relationships between GHG flux and BT in all stockpile treatments. There were significant ($p \leq 0.05$) correlations between N_2O emissions and BT, and CO_2 emissions and BT in the LS, USS and PSS biosolid treatments (Table 1). We detected no significant relationships between CH_4 flux and BT in any of the stockpiles.

There was no strong correlation between NO_3^--N or NH_4^+-N contents and GHG flux. However, there was a weak correlation between NO_3^--N and CH_4 flux for PSS and a weak correlation between NO_3^--N and N_2O emissions from LS.

There were no relationships between NH_4^+-N and flux of CH_4 or N_2O from either LS, USS and PSS. However, there was a good correlation between NH_4^+-N and CO_2 emissions from the LS.

3. 4 Annual GHG balance for three biosolid storage and management systems

Overall, annual GHG (CO_2-e) emissions were greatest from USS (65.2 kg Mg^{-1} dry biosolid), followed by PSS (54.8 kg Mg^{-1}) and were least from the LS (38.0 kg Mg^{-1}) **(Table 2)**. This values was reversed when annual GHG emissions (CO_2-e) were calculated on an area (hectare) basis as they were greatest in LS (393 Mg CO_2-e ha^{-1} yr^{-1}) followed by USS (195.3 Mg CO_2-e ha^{-1} yr^{-1}) and PSS (158.9 Mg CO_2-e ha^{-1} yr^{-1}).

Table 2. Estimated annual GHG emissions on a mass basis (kg CO_2-e dry Mg^{-1} yr^{-1}) and area basis (Mg CO_2-e ha^{-1} yr^{-1}) from the large stockpile (LS), unplanted shallow stockpile (USS) and planted shallow stockpile (PSS) and the associated C-e offset by the willow plantation (kg dry $Mg^{-1}$of biosolid or kg ha^{-1} yr^{-1}) at the Western Treatment Plant in Melbourne, Australia.

Stockpiles	Annual GHG emissions kg (CO_2 -e) dry Mg^{-1} of biosolid				Plant biomass (kg Mg^{-1} dry biosolid yr^{-1})
	CH_4	N_2O	CO_2	Total	
LS	0.64	12.1	25.3	**38.0**	-
USS	-0.006	45.6	19.5	**65.2**	-
PSS	-0.001	27.7	27.1	**54.8**	2.4
	Annual GHG emissions (Mg CO_2-e ha^{-1} yr^{-1})				Plant biomass (Mg ha^{-1} yr^{-1})
	CH_4	N_2O	CO_2	Total	
LS	6.6	124.8	261.7	**393.1**	-
USS	-0.02	136.8	58.5	**195.3**	-
PSS	-0.002	80.4	78.5	**158.9**	12

The GHG balance of the LS was dominated by CO_2 emissions (67%), whilst N_2O contributed to a smaller degree (32%) and CH_4 emissions were less than 2%. Conversely, in USS, N_2O

emissions accounted for 70% of the annual GHG emissions, whilst CO_2 contributed the remainder of emissions, and CH_4 was actually taken up by this stockpile. In the PSS, CO_2 and N_2O contributed almost equal amounts to the GHG balance and this stockpile was also a small CH_4 sink (Table 2). The PSS annually produced 2.4 kg tree dry biomass Mg^{-1} dry biosolid (or 12 Mg biomass per hectare), which equates to a C sequestration of 4.4 kg CO_2-e Mg^{-1}. This offsets approximately 8% of the 54.8 kg CO_2-e Mg^{-1} of GHG emissions that were emitted by this stockpile annually.

4. Discussion

4.1 CH_4, CO_2, and N_2O emissions from the three different biosolid management systems

Our direct measurements of GHG emissions from different biosolid stockpile options revealed that biosolids are a significant source for GHG. The different storage options changed the rate and contribution of the different GHG species but biosolids were a strong GHG source regardless of whether they were stored conventionally, in shallow stockpiles either unplanted or planted with trees. The main GHGs that contributed to the overall emissions balance were N_2O and CO_2, whilst emissions of CH_4 were either very low (LS) or negative creating a weak CH_4 sink (USS and PSS).

GHG emissions from any stockpile of organic material will largely depend on the characteristics of organic materials, the height and shape of the pile and environmental factors like moisture content and temperature (Boldrin et al., 2009; Peigne and Girardin, 2004). Anaerobic conditions inside a large conventional biosolid stockpile can lead to the production of CH_4, when labile organic material is decomposed by methanogenic bacteria. Hence, this can explain the CH_4 emissions from the LS. However, given that CO_2 emissions from the LS were almost 40 fold greater than CH_4 emissions it is likely that anaerobic conditions in the stockpile are either not prevalent or that large proportions of the produced CH_4 are oxidized before they reach the surface. Consequently, the bulk of the labile organic material in the LS was oxidised and reaches the atmosphere as CO_2. Both shallow biosolid stockpiles showed small CH_4 uptake rates. Methanotophic bacteria can consume CH_4 as an energy source under aerobic conditions (Hanson and Hanson, 1996). The shallow application of biosolid probably prevented anaerobic conditions developing, especially as biosolids generally have a low bulk density of 750-850 kg m^{-3}. Methane uptake is frequently observed in drier upland soils and represents the largest terrestrial sink for CH_4 (Dalal and Allen, 2008). The CH_4 uptake rate observed in both shallow biosolid treatments is similar to the uptake rates observed in urban (Livesley et al., 2010), agricultural (Livesley et al., 2008), savanna (Livesley et al., 2011) or forest ecosystems (Fest et al., 2009). Hence, shallow stockpiling leads to a decrease in CH_4 emission to the atmosphere by decreasing CH_4 production and/or increasing CH_4 oxidation, but this effect is small in the context of the overall GHG balance.

Nitrous oxide emissions are recognized as being strongly regulated by the availability of organic carbon and nitrogen substrates, and environmental factors, such as temperature and moisture (Peigne and Girardin, 2004). Nitrous oxide emissions were generally very high from all biosolid stockpile options and much greater than generally observed in natural systems, agriculture or even following biosolid applications as soil amendments (Dalal and Allen, 2008; Livesley et al., 2009; Thangarajan et al., 2013). In arable cropped soils N_2O emissions vary from <1 kg N_2O-N ha^{-1} yr^{-1} from leys and extensive pastures to >10 kg N_2O-N ha^{-1} yr^{-1} from sugarcane crops and intensively managed dairy pastures (Dalal et al., 2003). In comparison, the biosolid stockpiles had emission rates that were 20 times greater than the highest arable soil emission (Table 2), so they represent a large N_2O source. In agricultural soils N_2O emissions are often directly related to N-fertilizer or organic amendments and microbial transformation through nitrification or denitrification. Biosolids contain large amounts of labile nitrogen (Roy et al., 2011) and mineralization of this source leads to large concentration of NO_3^--N and NH_4^+-N. In our study, the biosolid NO_3^--N concentration was generally >200 mg N kg^{-1}, which is five to ten fold greater than that commonly reported in fertilized agricultural soils. Nitrate concentrations were considerably greater in the LS than in both USS and PSS. Available NO_3^--N is a substrate for denitrification, which might suggest that denitrification is not a dominant process in the LS stockpile, as this inorganic N substrate had accumulated without further denitrifier transformation. Biosolid NH_4^+-N content was greatest in USS, and this shallow stockpile also had greater NO_3^--N content than its planted counterpart. So despite being irrigated in summer by class C wastewater, the N uptake by willow trees appears to have reduced inorganic N contents in the biosolids and thereby potentially reduced N_2O emissions. This was in fact apparent, as PSS had less overall N_2O emissions than USS.

The other factors that influence nitrification and denitrification processes are moisture content and temperature. Moisture content increases nitrification rates and thereby nitrification derived N_2O emissions up to a maximum water holding capacity (%WHC) of approximately 60%, whereas N_2O production through denitrification generally is promoted at greater moisture contents (Dalal et al., 2003). The PSS was generally wetter than the USS, and yet had smaller N_2O emissions despite this and the available NO_3^--N and NH_4^+-N contents, which again might suggest that denitrification was not the dominant N_2O production process in the shallow stockpiles and that nitrification processes played an important role in N_2O production. In compost stockpiles oxygen and moisture contents influenced both nitrification and denitrification as moisture content and the supply of oxygen enhance microbial activities that produce N_2O (Peigne and Girardin, 2004). However, the exact mechanisms behind the N_2O emissions measured in our different biosolid stockpiles are not clear.

Greater N_2O emissions were observed from both shallow stockpiles as compared to the LS. This could be due to the lower depth of the shallow biosolid stockpiles, and therefore the greater surface area to volume of biosolid. A greater surface area to volume ratio would mean that a greater proportion of biosolid experiences the variations in temperature and moisture and has less distance for diffusion of GHGs from point of production to the atmosphere and for diffusion of oxygen into the stockpile (for aerobic processes such as nitrification). As such, the greater depth of stockpiles will generally slow the rate of organic matter decomposition and other microbially mediated processes. In cattle manure stockpiles microorganisms start to decompose (oxidize) organic matter from the top of the stockpile and then move downwards when fresh, labile substrate became less available at the surface (Hao et al., 2001). The greater N_2O emission rates from USS and PSS also support the proposal that microbially mediated processes may occur at faster rates in shallower stockpiles.

Carbon dioxide was the dominant form of carbon emission to the atmosphere in all biosolid stockpiles and the annual emission rates were comparable between the stockpiles, although USS had slightly lower CO_2 emissions compared to the others. Compared to soil based ecosystems the CO_2 emissions from the biosolid stockpiles were very high. Grasslands have an annual respiration rate around 16 Mg CO_2 ha^{-1}, croplands are slightly higher at 20 Mg CO_2 ha^{-1}, and the greatest soil respiration rates are commonly observed in tropical forests with around 46 Mg CO_2 ha^{-1} (Raich and Schlesinger, 1992). Hence, CO_2 efflux rates observed here are much greater with 58-78 Mg CO_2 ha^{-1} in the shallow stockpiles and 262 Mg CO_2 ha^{-1} in the large stockpile (Table

2), which is likely attributed to the large reservoir of labile carbon in the biosolids. The difference in CO_2 emissions between the LS and USS can be explained by the differences in current biosolid properties, moisture, temperature but perhaps most importantly differences in the availability of labile carbon. If the shallow stockpiles experience greater rates of microbial decomposition, then they are likely to reduce their stores of labile or more-available carbon more rapidly. Conversely, the large differences in CO_2 emissions between USS and PSS cannot be explained by differences according to stockpile size and surface area to volume ratio – as they are similar. It is more likely that these differences in CO_2 emissions are due mainly to the presence of willow root respiration, willow rhizosphere respiration and possibly the influence of irrigation with Class C water in summer months.

4.2 Relationship between GHG flux and environmental parameters of biosolid stockpiles

Environmental parameters of biosolid stockpiles that exhibit a strong relationship to the measured GHG fluxes could provide a simpler and cheaper opportunity to monitor change and therefore predict or indicate GHG emissions. Strong relationships between moisture content and/or temperature and GHG fluxes are often observed in many native and agricultural ecosystems as many microbial processes are strongly influenced by these parameters (e.g. Fest et al., 2009; Livesley et al., 2009). However, in our study we did not observe strong relationships between biosolid MC and GHG flux. In the LS, GHG are probably produced much deeper in the profile under aerobic or anaerobic conditions and then diffuse upwards to the surface and the atmosphere (Majumder et al., 2014). This would suggest that monitoring of environmental properties deeper in a stockpile may be required. Such monitoring at depth would also be beneficial for detecting high temperatures that may lead to combustions and stockpile burns, which once initiated are difficult to stop.

However, we did observe a weak relationship between biosolid temperatures at a 10 cm depth and both N_2O and CO_2 flux in the LS, USS and PSS. This suggests a weak seasonal pattern, in that microbial processes, and associated N_2O and CO_2 emissions, are greater in warm summer months and lesser in cooler winter months, which is consistent with first principles.

We did not observe any strong relationship between NO_3^--N or NH_4^+-N concentrations and N_2O flux. This could be due to only sampling the upper 10 cm which may not represent the profile position of greatest nitrification / denitrification activity and therefore N_2O production. Similarly, it could also be due to the fact that inorganic N pool size measures are not an adequate indication of turnover or transformation rates through those pools. For example, a large NO_3^--N pool may turnover only once a week, whereas a small NO_3^--N pool may be turning over several times a day, thereby leading to greater overall N_2O emissions (Murphy et al., 2003). Unless other environmental properties show greater correlation with GHG gas exchange from biosolid stockpiles it appears that direct GHG flux measures are required if accurate estimates of GHG emissions are to be produced.

4.3 Calculated annual GHG emissions from biosolid stockpile treatments and carbon offset from the shallow surface biosolid stockpile

The overall annual GHG balance of PSS was slightly less than that for USS. Both shallow stockpiles had a similar weak CH_4 uptake, but the planted shallow stockpile had a much lower N_2O emission, probably driven by a greater N-uptake by willow roots, and a slightly greater CO_2 emission, likely caused by the autotrophic respiration of willow roots. We estimated that the willow trees planted in PSS produced about 12 Mg of dry above-ground biomass per hectare, which equates to a CO_2 offset of 4.4 kg CO_2 Mg^{-1} dry biosolid. This estimate is comparable with other studies; Elowson (1999) studied different varieties of willow (*Salix viminalis*) and measured annual above ground biomass between 10 and 12 Mg per hectare, and noted that yield was dependent on factors such as planting density (Bullard et al., 2002) nutrient and water supply (Weih and Nordh, 2002). The total annual GHG emissions from the PSS were 58.4 kg CO-e Mg^{-1} dry biosolid. This means the 4.4 kg CO_2 Mg^{-1} dry biosolid that were sequestered by aboveground willow biomass offset only around 8 % of the net GHG emissions from shallow biosolid stockpile. Consequently, the carbon sequestration potential of biosolid plantation systems seems minimal. This is not because trees did not grow well in biosolids, 12 Mg ha^{-1} yr^{-1} is a very high rate of biomass accumulation, but because of the very high N_2O emissions and sizable CO_2 emissions that were caused by decomposition of the labile carbon and nitrogen in the biosolid stockpiles.

The direct measurement of GHG emissions from different biosolid stockpile options revealed that all biosolid stockpiles are a large source for GHGs. Labile forms of carbon and nitrogen are readily mineralized and produce much greater GHG emissions as compared to soil based systems. Some of this nitrogen is emitted in the form of N_2O and much of the labile carbon is emitted as CO_2, whilst CH_4 is a minor emission or is even taken up by shallow biosolids. Our study also revealed that spreading biosolid in shallower stockpiles does not decrease GHG emissions. On the contrary, a greater proportion of biosolids is exposed to the elements or diffusion pathways are shorter and consequently biosolids in shallow stockpiles had greater N_2O and similar CO_2 emissions. Planting trees in shallow biosolids lead to smaller GHG emissions compared to unplanted shallow biosolid stockpiles; but because of the greater exposure of biosolids in the shallower application they still had greater emissions than conventional stockpiles. The carbon sequestration by trees offset only 8% of the total emissions despite a sizable tree biomass accumulation, again confirming the large magnitude of GHG emissions. These results indicate that the management options in regard to reducing GHG emissions from biosolid stockpiles are very limited. Conventional stockpiles overall emitted less GHG compared to shallow stockpiles but they still had a huge emission footprint. The water industry needs to account for GHG emissions from biosolid storage and end-use in preparation for any national carbon-trading scheme. However, our data also indicate that alternate end-uses for biosolids, such as applications as soil amendments or substrates for bioenergy production should be explored as stockpiling of biosolids produces large GHG emissions.

Acknowledgements

The authors thank Kevin Gillett and Scott Laidlaw for help during the field based measurements. The study was supported by funding from the Australian Research Council (ARC) grants LE0882936, LP0883573 and DP120101735 and the Melbourne Water Corporation.

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