Title: Assessment and mitigation of the environmental burdens to air from land applied food-based digestate

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- In situ air pollution assessment of land applied digestate is performed.
- Environmental burden minimisation scenarios for digestate bio fertiliser presented.
- Food-based digestate show high ammonia volatilisation potential.
- Soil incorporated digestate effectively reduces NH₃ but elevates N₂O emissions.
- Managing digestate emissions mitigate both climate change and air pollution.

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Abstract (limit 150 words only)

Anaerobic digestion (AD) of putrescible urban waste for energy recovery has seen rapid growth over recent years. In order to ascertain its systems scale sustainability, however, determination of the environmental fate of the large volume of digestate generated during the process is indispensable. This paper evaluates the environmental burdens to air associated with land applied food-based digestate in terms of primary pollutants (ammonia, nitrogen dioxide) and greenhouse gases (methane and nitrous oxide). The assessments have been made in two stages – first, the emissions from surface application of food-based digestate are quantified for the business as usual (BAU). In the next step, environmental burden minimisation potentials for the following three mitigation measures are estimated - mixed waste digestate (MWD), soil-incorporated digestate (SID), and post-methanated digestate (PMD). Overall, the mitigation scenarios demonstrated considerable NH₃, CH₄ and N₂O burden minimisation potentials, with positive implications for both climate change and urban pollution.

Keywords: anaerobic digestion; bio fertilizer; digestate; environmental burdens; OFMSW

Capsule abstract: In situ monitoring and analyses demonstrate the role of post-processing in greenhouse gases and air pollution mitigation from food-based digestate use as bio fertiliser.

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1 1. Introduction

2 Digestate, the semi-solid residue obtained post biogas extraction in anaerobic digestion (AD), is 3 considered a vital source of organic matter and nutrients, especially nitrogen. It is increasingly being 4 applied as soil conditioner/amendment (on urban gardens, farmlands, recreation/sports grounds, fish 5 ponds, etc.), or alternatively for developing energy crops on brownfield/marginal land and sports turf production (WRAP, 2013). This is mainly due to its two attributes - one, for providing a low carbon 6 7 substitute for fossil fertilisers (Chambers and Taylor, 2013; WRAP, 2011); two, for restoring soil organic matter and for closed-loop nutrient recycling, especially mineral nitrogen (Fricke et al., 2007; 8 9 Karagiannidis and Perkoulidis, 2009; Möller and Stinner, 2009). Consequently, digestate field application 10 has been identified as a sustainable practice in terms of meeting the EU standards for good agricultural and environmental condition (GAEC) (RPA/Defra, 2012). However, with greater emphasis on strategies 11 12 for diverting biowastes from landfill and their sustainable re-utilisation through valorisation in AD, the 13 volumes of digestate are expected to increase rapidly (typical digestate represents 70-95% of the 14 feedstock volume) (Lukehurst et al., 2010). Digested slurries have been found to be significant sources of ammonia (NH_3) , methane (CH_4) and nitrous oxide (N_2O) emissions (Amon et al., 2006; Bacenetti et al., 15 2013; Nkoa, 2014; Wulf et al., 2002a), with potential implications for local-to-regional climate (NRC, 16 2002; Ravishankara et al., 2009) and human health (Peel et al., 2013). Nkoa's (2014) detailed review has 17 18 suggested that digestates can be considered as organic amendments (or organic fertilizers) only when 19 properly handled and managed.

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21 The content and quality of digestate depends largely on both the feedstock and the hydraulic retention 22 time (HRT) of the digester; usually longer HRT reduces the organic content owing to more effective 23 methanogenesis (Szűcs et al., 2006). Digestate quality is further affected by maturing in storage tanks 24 (Menardo et al., 2011). Rigid compliance criteria for Class I digestate have been set by the European 25 Commission (EC) and the British Standard Institution (BSI) (BSI, 2010; EC, 2014). Although the scale of AD operation dedicated to organic waste treatment is at an all-time high (and on the rise), there is still 26 27 relatively little published information on the composition and potential environmental behaviour of digestate, particularly from AD plants processing food wastes (Tiwary et al., 2015; Whelan et al., 2010). 28 29 Anaerobic digestion of slurry tends to increase ammoniacal-N concentrations, reduce carbon to nitrogen 30 ratios and increase pH, thereby increasing the risk of NH₃ losses during storage and soil application (Möller and Stinner, 2009). Inappropriate disposal of unstable digestate on land may lead to formation of 31 32 residual biogas, with potential health issues from exposure to its constituent non-methanic volatile 33 organic compounds and other hazardous air pollutants and odorous compounds (Palmiotto et al., 2014). 34

35 During AD, the majority of organic (slow release) nitrogen is transformed into readily available nitrogen 36 (RAN) (Defra, 2011), specifically for protein-rich feedstocks, including the organic fraction of the municipal solid waste (OFMSW)¹, dairy by-products and slaughterhouse waste (Kryvoruchko et al., 37 38 2009; Menardo et al., 2011). Typical total-N content of food-based digestate ranges between 5-8 kg m⁻³, 39 with about 60-80% of this present as RAN; the proportion of RAN to total-N in food-based digestate is nearly 40% higher than manure-based digestate (202 kg and 145 kg respectively for every 250 kg total-N) 40 (WRAP, 2011). Moreover, for digestate from kitchen waste feedstock RAN of as much as 99% of 41 corresponding Total-N has been reported (Furukawa and Hasegawa, 2006). Sensitivity analyses 42 43 conducted to assess the split share of digestate total-N (i.e. organic-N, NH_4 -N and NO_3 -N) on acidification potential have reported NH₃ and NO₃ as the main contributors to the enrichment of 44 pollutants in direct air and water environments respectively (Bernstad and la Cour Jansen, 2011; 45 46 Evangelisti et al., 2014). Free ammonia concentration is affected mainly by temperature, pH and total ammoniacal nitrogen (TAN) concentration (Chambers and Taylor, 2013). Whereas a number of 47 48 multivariate data analysis protocols using advanced sensor technologies have become available, the majority of these are currently (2014) limited to AD process monitoring; there are limited approaches for 49 digestate quality monitoring and they are all based on offline instrumentation (Oppong et al., 2012). 50 Minimum quality requirements for whole digestate, separated liquor and separated fibre have been 51 prescribed as part of a Publicly Available Specification (PAS 110)² standards in the UK (BSI, 2010). PAS 52 110 Clause 10 provides guidance on obtaining representative samples of all three types of digestates 53 54 (whole, fibre, liquor) via one or more sampling access points appropriately located in the digestate 55 production/storage system prior to its use.

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57 The knowledgebase involving environmental impacts from digestate land application is largely developed 58 from traditional approaches for cattle manure management, which requires incorporating the unique and 59 emerging characteristics of OFMSW digestate. From an environmental point of view there is an existing challenge of reducing the gaseous N-losses (NH₃, NO₂, N₂O) from digestate soil application to the fields 60 (Balsari et al., 2007; Misselbrook et al., 2005a; Nyord et al., 2008; Tiwary et al., 2015). This study aims 61 to determine and interpret the seasonal emissions profile to air from digestate slurry applied to urban soil. 62 The latter has been assessed through small plot experiments, applying digestate acquired from 63 64 community-scale AD operations. It evaluates the implications for climate change and urban pollution in terms of fitness for purpose of the available practice, including some proposed mitigation strategies. 65

¹ OFMSW is defined by the European Commission as "biodegradable park and garden waste, food and kitchen waste from household, restaurants, caterers and retail premises and comparable waste from food processing plants".

² PAS (Publicly Available Specification) is a sponsored fast-track standard driven by the needs of the client organisations in the United Kingdom, developed according to guidelines set out by British Standard Institute.

66 Preliminary outputs from field trials of in situ monitoring of soil-applied digestate for air emissions of N-

67 pollutants (NH₃, NO₂) and greenhouse gases (GHGs: CH₄, N₂O) are reported. These results feed into a

review of approaches to mitigate the environmental burdens while promoting re-utilisation potentials of

69 anaerobically digested slurry as marketable bio fertilisers.

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72 **2.** Materials and methods

73 2.1. Review of sampling and analytical techniques

A review of available techniques was deemed essential for designing a robust assessment methodology
 for evaluating the emissions from both the baseline and the responses to plausible mitigation strategies.

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77 2.1.1 Primary air pollutants

78 Several studies have reported monitoring of NH₃ emissions from land-applied manure in Europe (Gericke et al., 2011; Loubet et al., 1999; Misselbrook et al., 2005a; Nyord et al., 2012; Nyord et al., 2008), 79 80 Australia (Leuning et al., 1985), USA (Parker et al., 2013) and Canada (King et al., 2012). Inter 81 comparison of different monitoring techniques are also reported (NRC, 2002; Parker et al., 2013) (Misselbrook et al., 2005b). The following three broad categories of approaches have been applied for 82 83 estimating air pollutant emission rates from area sources: i) Micrometeorological mass balance 84 techniques, where fluxes are calculated from a large footprint using tower-based instrumentation (e.g., 85 gradient methods, eddy covariance); ii) Indirect methods, where ambient concentrations are measured and source emission rates are either back-calculated using dispersion models or using known transfer factors 86 87 from standards (also known as 'standard comparison' method; iii) Direct methods, where fluxes are measured from samples collected from the source using portable wind tunnels or flux chambers, followed 88 by colorimetric/FTIR spectroscopy. Among these, micrometeorological mass balance methods have been 89 90 found to provide more realistic estimates, thus widely used in field monitoring (Generemont et al., 1998; Nyord et al., 2012; Wilson and Shum, 1992), but limited to applications over larger source areas with 91 92 sufficient fetch for integration of emission rates. Standard comparison methods are popular owing to their 93 cost-effectiveness (Möller and Stinner, 2009; Wulf et al., 2002b) but are quite sensitive to surface 94 characteristics and meteorological conditions, requiring regular corrections to the fluctuations in the transfer factor applied in emissions estimates. In particular, such methods assume the transfer factors 95 estimated from standard plots to be valid for calculating the emission rates from the experimental plots, 96 97 overlooking the inconsistencies in micrometeorological conditions, especially the wind fields between the 98 standard and the experimental plots. Despite their limitations, portable wind tunnels and flux chambers 99 are often the only available, direct method for assessing air pollutant fluxes from small individual area sources. Theoretical principles of wind tunnel technique have been described in detail in the literature
(Loubet et al., 1999; Misselbrook et al., 2005b). The appropriateness and accuracy of portable wind
tunnels and flux chambers for quantifying area source emissions have been extensively discussed in the
literature (Fowler et al., 2001; King et al., 2012; Loubet et al., 1999; Misselbrook et al., 2005b; Nyord et
al., 2012; Parker et al., 2013).

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106 Qualitative assessment of the cost-benefits of the different monitoring techniques have also been reported (see for example (Gericke et al., 2011; Misselbrook et al., 2005b)). For small-plot comparative 107 108 measurements, a wind tunnel system is recommended, albeit with a caveat of its tendency to modify the temperature at the emitting surface relative to the ambient conditions owing to canopy effect (Braschkat 109 et al., 1993; Misselbrook et al., 2005b; Nyord et al., 2012), thereby influencing the emission rates. 110 Application of wind tunnel technique is thus far best suited for making comparative measurements for 111 112 treatments imposed on small plots and less representative for estimating the absolute air emissions from 113 large area sources.

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115 2.1.2. Greenhouse gases

116 Compared to monitoring of primary air pollutants, there appears to be a greater consistency in the 117 reported literature on monitoring of greenhouse gases (GHG) from area sources. The majority of the 118 studies have applied closed chambers (static or mobile) for sampling of N_2O and CH_4 , followed by 119 concentration estimations using gas chromatography (Amon et al., 2006; Wulf et al., 2002a). With closed 120 chambers, however, reportedly there is an issue with negative feedback of increasing gas concentration in 121 the chamber on the rate of diffusion of the gases, implying that the rate of release is often very high 122 immediately after land application.

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125 2.2. Sampling and analysis

126 2.2.1 Experimental design

127 A dedicated wind tunnel experimental set up was developed following Lockyer (1984) and Loubet et al. 128 (1999), comprising of an upwind-downwind gas sampling system and an air extractor (fitted with an 129 anemometer to monitor the average wind speeds through the tunnel canopy). The front portion of the 130 wind tunnel was fabricated using transparent polycarbonate material covering 1 m² (2 m long x 0.5 m 131 wide), offering exposure to direct sunlight and ensuring negligible temperature interference from the 132 tunnel to the treated surface area. Three separate wind tunnels were operated simultaneously in parallel 133 (Fig. 1) to acquire statistically representative samples (Misselbrook et al., 2005a; Nyord et al., 2012). Air was drawn from the upwind/downwind sampling ports located on top of the tunnel into impinger tubes containing the absorbing media through three sets of polytetrafluoroethylene (PTFE) tubing (approximately 4 mm internal diameter) at a flow rate of 3 l min⁻¹ using an arrangement of two manifolds and suction pumps. For GHG, only the downwind port of the middle tunnel was used to draw the sample from an air-tight chamber inserted into the soil to a depth of 10 cm.

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140 2.2.2 Field sampling

All land application experiments were conducted at a field site representative of tropical climes, located at 141 142 The Energy and Resources Institute (TERI) campus (suburbs of New Delhi, 28.45 °N, 77.03 °E), India. Three wind tunnels, each covering an exposed area of 1 m^2 , were operated in parallel on a 4m x 4m plot 143 (Fig. 1), and predominantly composed of sandy loam soil (pH - 5.5, organic matter content (%) - 3.7). 144 The wind tunnels were positioned such that the canopy inlets were located at the upwind edge of the plots 145 and they remained in the same position for the entire duration of each experiment. To avoid cross-146 interference of emissions between the neighbouring wind tunnels care was taken to restrict the spread of 147 fresh digestate slurry within the exposed portion of each tunnel using a watering can. The amount of 148 digestate spread on different plots was volume-limited to 0.02 m³ (i.e. 20 L), with a spread area of 1 m² 149 and application thickness of 2 cm per plot. All the experiments were conducted with no precipitation 150 151 recorded within the first 24 h following digestate application.

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153 Air pollutants (NH₃, NO₂) were sampled over 6 consecutive days following digestate application based on 154 the literature (Nyord et al., 2012; WRAP, 2011). Although previous experiments using digested cattle slurry have reported NH₃ emissions to cease after 48 h (Amon et al., 2006), a relatively longer sampling 155 period was chosen for food-based digestate, potent to exhibit longer emission patterns owing to higher 156 RAN (Chambers and Taylor, 2013; Whelan et al., 2010). A quality assurance run was performed to 157 establish the sampling protocols for NH₃ using two-serially connected impinger tubes to the downwind 158 port. This experiment showed that less than 2% of the total NH₃ trapped during the sampling reached the 159 160 second impinger tube, which confirmed the emissions were insufficient to fully saturate the absorbing media in the first impinger tube. Therefore, for all subsequent experiments only one impinger tube was 161 162 used for the entire sampling. During each experiment, the impinger tubes filled with absorbing media, and connected to the upwind/downwind sampling ports of all the three wind tunnels, were simultaneously 163 exposed continuously at a stretch for 4 h (corresponding to sampling medians of 2, 26, 50, 74, 98 and 122 164 165 h).

166

Monitoring of greenhouse gases (CH₄, N₂O) was performed from an air-tight chamber connected to the downwind sampling port of the middle wind tunnel owing to logistical limitation in simultaneous operation of gas chromatograph. Following land application, CH₄ was monitored for up to 7 days on a daily basis (Wulf et al., 2002a); N₂O was monitored for up to 30 days at a sampling interval of 0, 1, 2, 3, 5, 9, 16, 23 and 30 days, with reduced sampling frequency beyond the first week as per the literature (Amon et al., 2006; Wulf et al., 2002a).

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174 2.2.3 Analysis

175 Methodological details of the analysis adopted for different digestate parameters (dry matter (DM) 176 content, pH, total Kjeldahl N (TKN) content, total ammoniacal N (TAN) content, etc.) are provided in 177 Table 1. Analyses of primary air pollutants followed the standard practice for quantifying ambient air 178 concentrations by bubbling a known volume of air through the impinger tubes filled with absorbing media and connected to the upwind/downwind sampling ports of the tunnels. NH₃ was quantified through the 179 Indophenol method (Method 401, Air Sampling and Analysis, 3rd Edition, (CPCB, 2011)) using a dilute 180 181 solution of sulphuric acid as absorbent to precipitate the airborne ammonia as ammonium sulphate 182 followed by its colorimetric analysis by reaction with phenol and alkaline sodium hypochlorite to produce indophenol. NO2 was quantified through the modified Jacobs & Hochheiser method (IS5182 Part 6, 183 Methods for Measurement of Air pollution: Oxides of nitrogen (CPCB, 2011)) by bubbling the sample 184 through a solution of sodium hydroxide and sodium arsenite to convert the airborne NO₂ into nitrite ion 185 (NO_2^{-1}) . In the subsequent step, this was colorimetrically analysed by reacting with phosphoric acid, 186 187 sulphanilamide and N-(1-naphthyl)-ethylenediamine di-hydrochloride (NEDA). The emission per sampling period was calculated as the product of the volume of air passing through the tunnel and the 188 difference in outlet and inlet air concentrations. For each measuring period, the background pollutant 189 190 concentration from the inlet located on the upwind face of the tunnel was estimated and subtracted from 191 the cumulative concentration estimated from the port located on the downwind face of the exposed area.

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The GHGs were analysed by means of a gas chromatograph (GC-5700 series, Nucon Engineers, New Delhi) using a 1.8 m (~6 ft) long Poropak-Q column with thermal conductivity detector (TCD). The injector port, the detector and the oven were operated at temperatures of 40, 40 and 35°C respectively. Argon was used as a carrier gas at a pressure of 1.8 kg cm⁻². One ml of gas sample was injected using a micro syringe into the gas chromatograph for analysis.

- 198 199
- 200 2.3 Scenario analysis

The following scenarios were developed and tested sequentially using the experimental facility. Details of the physico-chemical properties of the digestate used in this analysis are presented in **Table 2**. For primary air pollutant monitoring (NH₃, NO₂), the cumulative emissions for the different scenarios were estimated as arithmetic means of three replicates (**Fig. 1**), as it is considered more robust (and less biased) for small numbers of replicates (Wulf et al., 2002a). The overall emission trends were obtained by fitting regression curves to the experimental data in SigmaPlot v12.5 (Systat Software Inc.).

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208 2.3.1 Business as usual

As a first step, assessments were conducted for the baseline emission patterns (BAU) following land application of digestate obtained from processing 100% OFMSW in a two-stage AD plant, available at the study site. The digestate was relatively fresh when land applied, keeping the approach consistent with the growing emphasis on reducing the storage time of digestate used as soil amendments, in order to avoid nutrient (mainly RAN) and carbon loss.

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215 2.3.2 Mixed-waste digestate

216 Typically, mixed-waste feedstock (with higher C/N ratio) have tendency to improve biogas yield and lower NH₃ release potentials from digestate. Co-digestion of OFMSW with cattle manure is commonly 217 218 adopted in wet digestion (Banks et al., 2011). On the other hand, co-digestion of waste having high N-219 content (food waste, vegetable waste, food processing industry waste and slaughterhouse waste) with 220 waste paper (typical mix of 95% to 5% respectively) is proposed for controlled dry digestion (Li et al., 221 2011; Takata et al., 2013), owing to its collateral benefits of adjusting the C/N ratio of the medium and regulating the accumulation of both NH_3 and VFA in the reactor. As the first mitigation measure, 222 performance of a mixed waste digestate (MWD), obtained following co-digestion of 70% OFMSW (food, 223 fruit and vegetable waste) with 30% cattle dung, was evaluated to optimise the earmarked emissions. 224

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226 2.3.3 Soil incorporated digestate

Uniform application of digestate slurry near or under the soil surface is recommended as an environmental best practice in the literature (Amon et al., 2006; Nyord et al., 2012). However, 'sub-surface incorporation', has demonstrated mixed results in abatement of gaseous emissions. While it positively mitigates NH₃ emissions (Chambers and Taylor, 2013; Nyord et al., 2012; Wulf et al., 2002b), it tends to exacerbate the GHG emissions under anaerobic conditions (CH₄, N₂O) (Möller and Stinner, 2009; Nkoa, 2014; Wulf et al., 2002a). The proposed mitigation measure of soil incorporated digestate (SID) involved shallow injection (5-7 cm below ground) of the BAU digestate, followed by its immediate

soil incorporation based on the best available technique (BAT) recommended in the literature (Brizio andGenon, 2010).

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237 2.3.4 Post-methanated digestate

238 Typically during the first 2 months of digestate storage post-methanation, up to 15% additional CH₄ yields have been reported (Balsari et al., 2013; Menardo et al., 2011; Weiland, 2010). However, digestate 239 240 storage during post-methanation also have collateral influence on NH₃ emissions, owing to high ammonium nitrogen (NH₄-N) concentration (Whelan et al., 2010). Previously reported NH₃ emission 241 rates ranged between 2.06 and 4.44 g NH₃ m⁻² and between 7.89 and 14.6 g NH₃ m⁻² from stored, whole 242 digestate and from digested liquid fraction respectively (Gioelli et al., 2009). The post-methanated 243 digestate (PMD) for this study was obtained after maturing the BAU digestate into a 150 L concrete tank 244 with a floating dome for 45 days. 245

- 246 247
- 248 **3** Results and discussion

The sampling and analyses steps described above were repeated to obtain the corresponding emissions for NH₃, NO₂, CH₄ and N₂O in order to evaluate the environmental performance of the proposed mitigation scenarios MWD, SID and PMD with reference to the BAU. The following sections describe the observed trends as well as their seasonal variations, if any; these are discussed in the context of developing effective digestate handling and management strategies to achieve reduced environmental burdens and enhanced economic values, the latter in terms of improved nutrients and organic matter reutilisation.

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258 *3.1 Emissions trends*

259 3.1.1 Ammonia emissions

260 The NH₃ emissions for all the scenarios showed a common trend of highest emissions within the first two days and negligible emissions beyond the four-day threshold (Fig. 2a), which agrees with previous 261 262 studies (Amon et al., 2006; Möller and Stinner, 2009; Wulf et al., 2002a). Preliminary results suggest that digestate surface application leads to significant losses of NH₃ to air over a short span during the first 263 week, with the business as usual having the highest cumulative NH₃ emissions following land application, 264 265 estimated to be over 65% of the applied TAN (Fig. 2b). Compared to this, application of mixed feedstock 266 digestate and post-methanated digestate had cumulative emissions around 45% and 35% of applied TAN 267 respectively, resulting in over 35% NH₃ reductions over the business as usual from these interventions.

However, the maximum NH_3 abatement of around 85% was achieved from slurry soil incorporation immediately following application; the cumulative emissions estimated in this case was around 10% of the applied TAN and negligible NH_3 emissions were observed from the second day onward (< 1% of

TAN), which was along the lines of previous reportings (Nyord et al., 2012; Wulf et al., 2002a).

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274 3.1.2 Nitrogen dioxide emissions

275 The majority of AD literature has extensively reported on NH₃ emissions whereas NO₂ emissions from 276 digestate application are not adequately accounted for in the emissions inventories. NO₂ emissions from soil amended plots are considered highly uncertain, and strongly influenced by the soil microenvironment 277 (MNP, 2007); estimates from a previous digestate assessment study suggest it to be up to 15% of the NH₃ 278 279 emissions in the Netherlands (de Vries et al., 2003). Results from our study showed overall trends for 280 NO₂ emissions similar to NH₃, with BAU having the largest cumulative emissions, followed by MWD while SID showed negligible NO_2 emissions (Fig. 3). The rate of emissions for both BAU and MWD 281 were very feeble past 24 h from land treatment, and their respective cumulative emissions were estimated 282 283 within 10% and 4% of TAN.

284

285 3.1.3 Methane emissions

286 Compared to NH_3 the observed CH_4 emission intensity was noted to be relatively short-lived for BAU, 287 with a steep decline in emissions from day 3 onwards (Fig. 4). Nevertheless, based on our analysis, in the 288 initial 1-2 days from land application, BAU had the highest CH₄ emissions intensity, followed by MWD. PMD, despite showing similar emissions trend temporally, had a much reduced intensity (up to 56% 289 lower) compared to the BAU. This is mainly attributed to residual CH₄ extraction from post-methantion; 290 reported estimates of residual CH_4 potentials during digestate maturing/long term storage (up to 180 day) 291 vary, ranging from 5-15% to 12-31% of total methane production (Weiland, 2003). These variations are 292 293 linked to the feed quality, the organic loading rate (OLR) and the HRT of the AD process, as well as the 294 moisture content of the digestate itself, typically reported residual CH₄ potential for animal manure, energy crops and food industry waste range between 2.88 and 37.63 L kg⁻¹ volatile solids (Menardo et al., 295 296 2011). The steep hike in emissions in the initial phase (within 1-2 days) post-application for BAU, MWD 297 and PMD is mainly attributed to the readily available dissolved CH₄, produced during storage of the substrate. On contrary, SID showed a lower emission intensity in the first 24 hour, peaking only after 2 298 299 days of land application. These trends of delayed peaking of CH₄ from injected slurry is also found in 300 previous monitoring campaigns (Wulf et al., 2002a) and can be mainly attributed to kick-starting of sub-301 surface anaerobic degradation of VFAs through methanogenesis under humid conditions.

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303 3.1.4 Nitrous oxide emissions

Nitrous oxide is formed as an intermediate product of both nitrification and de-nitrification. Previous 304 305 studies have reported strong increase in N₂O emissions from mitigation strategies for reducing NH₃ 306 volatilisation involving either application of liquid digestate, typically with a narrow C/N ratio and high soil infiltration levels (Möller and Stinner, 2009), or injection and soil incorporation of digestate (Wulf et 307 al., 2002a). Indirect N₂O production from emitted NH₃ has been considered a potential indirect 308 contributor to global warming (Wulf et al., 2002a), with approximately 1% of NH₃-N assumed to be re-309 310 emitted to the atmosphere as N_2O-N (IPCC, 2001). However, this mechanism was negated as a possible source for N₂O in our experiments and all N₂O was attributed to direct emissions, given the use of wind 311 tunnel and the timescale of samples collected. The BAU and MWD showed similar levels of emissions, 312 PMD had relatively lower emissions but SID showed a peculiar, and quite contrasting emission trend, 313 with increasing levels of emissions recorded about two weeks post land application (Fig. 5), which is also 314 reported in previous studies (Möller and Stinner, 2009; Nyord et al., 2008). The background N₂O 315 emissions from the bare soil have also been shown in this figure for reference. 316

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319 *3.2. Seasonal effects*

320 There is evidence of increased air emissions following digestate soil application on environmental factors, 321 such as ambient temperature, wind speed and precipitation (Chambers and Taylor, 2013; Nyord et al., 2012; Parker et al., 2013; Peel et al., 2013). This section reports outcomes of the air emissions evaluated 322 for two contrasting periods: summer (August – October) and winter (January – March) (Table 3). Based 323 on the outputs from the monitoring experiments, potential environmental burdens for NH_3 , NO_2 , CH_4 and 324 N₂O to air were estimated over the two seasons as a function of the fresh matter digestate mass applied to 325 326 soil for the BAU, MWD and SID scenarios (Table 4). Distinct seasonal characteristics influencing the emissions have been identified below. 327

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Sunlight hours - Our results showed strong dependence of the monitored emissions on sunlight hours; the observed trends as $NH_3 \gg N_2O > CH_4$, whereas NO_2 showed an inverse dependence. For all the trace gases the cumulative emissions remained unaltered and the effect of cooler and moist periods during winter mainly impeded their release rates, as reported in previous studies (Wulf et al., 2002a). NO_2 emissions were marked with large fluctuations and were found to be higher during overcast winter months (typically with average ambient temperature around 10°C and less than 2 hours of direct sunlight on the field plots). 336

Wind speed - In previous studies, wind speed has been reported as one of the parameters with the greatest
influence on NH₃ emissions from slurries (Misselbrook et al., 2005a). As followed in this study, the wind
tunnel set up reportedly provides a more robust wind-sensitive NH₃ emissions estimates (Rong et al.,
2009). The contrasting wind micro-environment recorded over the two seasons, with up to 75% reduction
in winter over summer (**Table 3**), seems to have resulted in large differences between the observed
emissions, especially for NH₃.
Soil moisture - Lower wind speed during winter resulted in sustained build-up of humid conditions inside

the tunnels, enhancing the soil moisture content (**Table 3**). This is turn resulted in poor soil respiration, contributing to reduced emissions during this period. On contrary, NH₃ losses were intensified during summer when slurries were applied to dry soils under warm weather conditions. For CH₄, the dry conditions facilitated formation of crusts on whole digestate, resulting in possibility of some anaerobic release of residual CH₄. Also, in case of SID, the increased soil temperature triggered sub-soil anaerobic processes, resulting in relatively higher N₂O emissions over summer.

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352 4 Conclusions and future directions

353 This study demonstrates application of simultaneous *in situ* monitoring of air pollutants (NH_3 , NO_2) and 354 GHGs (CH₄, N₂O) following land application of digestate as bio fertiliser. The baseline emissions from 355 the business as usual (BAU) have been evaluated in the first step, followed by assessment of the 356 corresponding environmental burden minimisation potentials of three proposed mitigation measures mixed waste digestate (MWD); soil-incorporated digestate (SID); post-methanated digestate (PMD). Our 357 results show the proposed mitigation measures to be effective over BAU: NH₃ emissions are considerably 358 reduced from MWD and PMD (by up to 35% and 43% respectively) and significantly reduced from SID 359 360 (by up to 85%). However, delayed elevation peak for N_2O in case of SID, primarily attributed to subsurface denitrification, showed marginal increase in emissions over BAU (by up to 2%). On the other 361 362 hand, PMD effectively reduced CH₄ emissions (by up to 55%) with inconsiderable influence on other emissions. Nonetheless, we acknowledge these outcomes as specific to food-based digestate; the 363 364 effectiveness of the proposed mitigation strategies to digestates arising from other feedstocks will vary, primarily owing to their different physico-chemical characteristics. It is also noteworthy that the results 365 are based on digestate characteristics from our pilot-scale anaerobic reactor, which may differ for other 366 367 digestate characteristics depending on the type of substrate and the type of AD process adopted.

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The study highlights some paradoxical future sustainability concerns for the voluminous amounts of digestate bound to be inadvertently generated from increased processing of OFMSW using AD. It warrants timely intervention for developing adequate strategy for post-AD handling and management of digestate, ideally as a marketable product (e.g. bio fertiliser) to the urban allotment/vegetable gardeners and to the wider farming communities. In addition, it solicits consideration for more advanced methods of digestate processing and reutilisation, including - dewatering, storage, composting, curing, exploiting alternative applications in construction/regeneration activities, etc.

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377 Further, development of a practical software tool quantifying the emissions from digestate soil applications would facilitate sustainable digestate management practice on a routine basis. In this respect, 378 379 our preliminary work on meteorological consideration can serve as useful stepping stones. It is 380 noteworthy this study reported baseline emissions from bare plots, assuming the soil amendments are meant to prepare the land for cropping. Although some literature reports on the long term emission trends, 381 incorporating the responses from planted vegetation (see for example, Moller and Stinner 2009), these are 382 primarily for rural setting, and a more comprehensive study on the usage of digestate as soil amendment 383 384 in the urban context is recommended as a natural next step study in order to develop full appreciation of 385 the coupled soil-vegetation effects.

386 387

388 5 Acknowledgements

This research was supported by a Marie Curie International Outgoing Fellowship within the 7th European Community Framework Programme (FP7/2007-2013) under grant agreement no. 275861. The paper reflects only the author's views and that the European Union is not liable for any use that may be made of the information contained herein. Contributions from the field staff at TERI, India are also acknowledged for their help during the sampling and analyses activities. We would also like to acknowledge the invaluable contributions from the anonymous reviewers in further improving the quality of this paper.

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Table 1.

Parameter	Method/Approach	Literature source		
Dry Matter (% FM)	Oven drying at 105 °C	(APHA, 2005)		
Organic Matter (%)				
pН	Digital pH meter (accuracy of ±0.01 pH unit)	(APHA, 2005)		
TKN in digestate	Digestion of sample with H_2SO_4 and use of Kjeldahl	(APHA, 2005)		
$(g (kg FM)^{-1})$	apparatus for distillation			
TAN in digestate	Distillation method	(APHA, 2005)		
$(g (kg FM)^{-1})$				
CH ₄ , N ₂ O in gaseous samples	Gas Chromatograph (NUCON 5700) equipped with auto sampler and a thermal conductivity detector and 6 feet long Poropak Q stainless steel column	(APHA, 2005)		
NH ₃ , NO ₂ in gaseous samples (μ g m ⁻³)	Shimadzu spectrophotometer (UV1700)	(CPCB, 2011; Misselbrook et al., 2005b)		

TKN = Total Kjeldahl nitrogen; TAN = Total available nitrogen (as ammonia)

Table 2.

	BAU	MWD	PMD	
рН	8.5	8.2	8.7	
Dry matter (% solids v./v.)	4.3	5.6	3.2	
Organic matter (%)	18.5	16.2	15.7	
Total N (g)	147.2	120.6	128.7	
RAN (g)	118.8	87.8	106.5	
Total S (SO ₃ , g)	8.8	16.5	8.7	
Specific gravity (kg m ⁻³)	0.99	0.98	0.99	
Fresh matter (g)	19.8	19.6	7.3	
Digestate volume (L)	20	20	20	

(Note: BAU - 100% OFMSW; MWD - 70% OFMSW+30% cattle dung, v./v.; PMD – matured BAU)

Table 3.

	Avg. Air Temp.	Avg. Soil Temp.	Avg. Wind Speed	Soil moisture	Precipitation(mm)	Qualitative comments
	[z=5cm]	[z=-5 cm]	[z=25cm]	(%)		
	(°C)	(°C)	(m s ⁻)			
Summer experiments (Aug – Oct	39	31	2	10	0.8	dry/sunny
2013) Winter experiments	11	7	0.5	45	5	humid/ foggy
(Jan – Mar 2014)						

Table	e 4 .
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Feedstock type	NH ₃		NO ₂		CH ₄		N ₂ O	
	S	W	S	W	S	W	S	W
BAU	5.05	4.25	0.75	0.90	1.3E-02	1.0E-02	8.5E-04	4.2E-04
MWD	2.69	1.55	0.30	0.45	1.1E -0 2	7.0E-03	6.3E-04	3.5E-04
SID	0.79	0.27	0.04	0.05	1.2E-02	9.0E-03	8.6E-04	5.7E-04

S=summer (~40°C, dry/sunny); W=winter (~10°C, humid/foggy)







a)

















Fig. 5