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#### Laboratory assessment of ammonia emission after soil application of treated and untreated manures

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1 Laboratory assessment of ammonia emission after soil application

#### 2 of treated and untreated manures

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#### 24 Summary

25 Ammonia (NH<sub>3</sub>) volatilization from soil-applied manure not only causes 26 environmental pollution, but also reduces the fertilization value of the manure. 27 Anaerobic digestion and solid/liquid separation alter the physical and chemical 28 characteristics of slurry, which affect NH<sub>3</sub> emissions after application. This study 29 measures potential laboratory NH<sub>3</sub> losses emissions from different manures, 30 untreated pig slurry, and the liquid fractions of each untreated and digested slurry, 31 after their application to two different soil types. The experiment was carried out 32 in dynamic chambers using a photoacoustic infrared gas analyzer to directly 33 determine the NH<sub>3</sub> concentration in the air stream.

34 The estimated values of N emitted for surface-applied, untreated pig slurry 35 were  $0.26 \pm 0.064$  mg per mg of applied total ammoniacal-nitrogen (TAN). For 36 the liquid fractions of pig slurry and digested pig slurry, results were  $0.13 \pm 0.064$ 37 mg/mg and  $0.16 \pm 0.064$  mg/mg, respectively. Initial NH<sub>3</sub>-N emission rates from surface-applied, untreated pig slurry were higher than those measured for either 38 39 liquid fraction; in the case of the untreated pig slurry, half was emitted in the first 40 4.9 hours of measurement. Silty-loam soil showed a higher N emission than did 41 loam soil with surface-applied slurries. This result was probably due to the higher 42 infiltration rate of loam soil, even offsetting the effect of its high soil pH. 43 Immediate manure incorporation into the soil was shown to reduce NH<sub>3</sub> emissions 44 by 82%.

Results demonstrated that a method combining dynamic chambers with a
photoacoustic gas analyser was as reliable as the widely-used acid traps method.
Moreover, the direct measurement with the gas analyser permits an increasing

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temporal resolution that gives a high-quality description of the NH<sub>3</sub> emission dynamic.

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51 Key words: Ammonia emission; photoacoustic spectroscopy; fertilizer;
52 manure; anaerobic digestion; solid/liquid separation.

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#### Introduction

Animal husbandry and manure management accounts for more than 80% of total ammonia (NH<sub>3</sub>) emissions from European agriculture, estimated as 2902 Gg per year; land application of manure, especially slurry, contributes a large proportion of these losses, and represents between 30% and 40% of total emissions from livestock production (Hutchings *et al.* 2009).

60 Ammonia volatilization reduces the manure-nitrogen (N) use efficiency in 61 crop production and increases the uncertainty of crop N balance and optimal 62 fertilizer N rate calculations (Sommer et al. 2004). From an environmental 63 perspective, the loss of NH<sub>3</sub> to the atmosphere causes negative effects through 64 acidification and eutrophication of natural ecosystems, as well as via secondary particulate matter formation (Sutton et al. 1998; Goebes et al. 2003). For these 65 66 reasons, international and European agreements have established regulations to 67 limit this pollutant, which requires calculating national inventory levels of the contribution from agriculture to total emissions (Erisman et al. 1998). These 68 69 inventories are based on emission factors that, in the advanced method of 70 calculation, are also specific for the emissions produced during manure spreading.

71 Ammonia emissions from manure applied to the soil are shaped primarily 72 by physical and chemical processes, and secondarily by biological ones. All of the 73 following have been shown to cause variation in the loss amount from 74 approximately nil to 60% of total ammoniacal-N (TAN) applied (Sommer et al. 75 2003): (i) environmental conditions (i.e. wind speed, temperature, precipitation, 76 humidity), (ii) manure properties (i.e. dry matter content, viscosity, pH, TAN 77 content), (iii) soil properties (i.e. pH, cation exchange capacity, porosity, 78 infiltration rate), (iv) interaction between slurry and soil, as well as (v) distribution 79 method and rate of application. Under constant environmental conditions, the 80 pattern of NH<sub>3</sub> volatilization shows high loss rates immediately after slurry 81 application due to the high initial concentration of TAN and the pH increase in the 82 manured-soil surface (Søgaard et al. 2002). The volatilization rate then decreases 83 rapidly as a result of the NH<sub>4</sub><sup>+</sup> concentration reduction in the fertilized soil surface 84 from volatilization, infiltration, and nitrification. The pattern of NH<sub>3</sub> volatilization 85 after soil application of slurry is usually described in the literature by the 86 Michaelis-Menten type equation (Sommer & Ersbøll 1994; Søgaard et al. 2002; 87 Misselbrook et al. 2005).

Anaerobic digestion, solid/liquid separation of liquid manure, and other manure treatments may also influence gaseous losses because they change the physical and chemical characteristics of manure, and affect the extent of emissions after field spreading (Amon *et al.* 2006; Sommer *et al.* 2006, Petersen & Sørensen 2008). Solid/liquid separation reduces the dry matter in the liquid portion of the slurry, which boosts slurry infiltration. Anaerobic digestion increases TAN content and manure pH, which raises the NH<sub>3</sub> volatilization

potential, and decreases dry matter content which increases slurry infiltration rates
and decreases NH<sub>3</sub> emissions.

97 The effect of manure and soil properties on NH<sub>3</sub> emissions has been 98 extensively investigated in field (Thompson & Meisinger 2002; Sommer et al. 99 2004; Misselbrook et al. 2005) and laboratory studies (Amon et al. 2006; Sommer 100 et al. 2006). For laboratory assessment, the dynamic chamber is the most utilized 101 method, in which NH<sub>3</sub> emitted from manure is collected in acid solutions 102 (sulphuric, boric, or ortho-phosphoric) and determined via titration (Le Cadre et 103 al. 2005). Recently, slurry infiltration (Sommer & Jacobsen 1999), slurry type 104 (Sommer et al. 2006), urease inhibitor (Watson et al. 2008), and no-till (Rochette 105 et al. 2009) effects on potential NH<sub>3</sub> emissions were investigated using dynamic 106 chambers coupled with acid traps. Nevertheless, using acid traps is time-107 consuming (e.g. acid solution collection, separate laboratory analysis for NH<sub>4</sub><sup>+</sup> 108 determination), with variable and, in general, low temporal resolution, especially when small NH<sub>3</sub> amounts are emitted. This second drawback leads to information 109 110 loss, especially during the first hours after fertilizer application when emission 111 rates vary rapidly.

Infrared photoacoustic spectroscopy has recently become popular for air sample analysis of several gases (e.g. CO<sub>2</sub>, N<sub>2</sub>O, CH<sub>4</sub> and NH<sub>3</sub>) due to its high accuracy and selectivity (Hoy 1995; Berg *et al.* 2006; Dinuccio *et al.* 2008). Commercial applications of this technology allow automated air sampling, high temporal resolution of measurements, and direct data recording and display of electronic datasets. Mathematical descriptions of the emission dynamics can consequently be performed more adequately. However to-date, few studies exist

on the accuracy and reliability of using photoacoustic spectroscopy with dynamic
chambers for NH<sub>3</sub> emission assessment.

In the present work, we report the results of a laboratory assessment of NH<sub>3</sub> emission after soil application of different treated and untreated pig slurry (i.e. no treatment, solid/liquid separation, anaerobic digestion followed by solid/liquid separation) using a system composed of dynamic chambers and a photoacoustic infrared gas analyser. The reliability of this method was evaluated via comparison to the most commonly used acid traps method.

#### Materials and methods

#### 129 Treatments and soils

130 Three manure treatments were compared in the experiment: untreated pig 131 slurry (Untreated S), the liquid fraction of untreated pig slurry (Untreated S 132 liquid), and the liquid fraction of anaerobically-digested pig slurry (Digested S 133 *liquid*). We sourced the pig slurry samples from a house for grower-finisher heavy 134 pigs (up to 160-180 kg/head) raised on a fully slatted-floor. Anaerobic digestion 135 was performed in continuously-fed laboratory reactors under mesophilic 136 conditions (38-39 °C) with a hydraulic retention time of 26 days and an organic loading rate of 1.35 kg VS/m<sup>3</sup>/d. The solid and liquid fractions of untreated and 137 138 digested slurries were separated using a laboratory centrifuge at 7000 rpm 139 (Mantovi et al. 2010). All manure types were stored for a total of 120 days in 50 L 140 covered tanks at ambient temperatures to simulate farm storage before spreading. 141 The different manures were then analysed for their main physical and chemical 142 characteristics (Table 1) and stored at 4°C until the start of each trial.

143 We collected the soil used in the experiment during June 2008 from the 144 tilled top 20 cm layer of two arable soil types in the western Po River Plain 145 (Northern Italy). The two soils were labelled *Loam* and *Silty-loam* based on their 146 texture classification (Soil Survey Staff 1998) (Table 2). The soils were air dried 147 and sieved at 5 mm to remove plant debris. A sample of each soil was ground (2 148 mm) prior to analysis for soil characterization. Loam and Silty-loam soils have a 149 sub-alkaline and a sub-acid reaction, respectively. While both of these soils were 150 poor in organic matter and total N content, each had a different cation-exchange 151 capacity (Loam soil: low; Silty-loam: medium) (Sposito G. 1989; Bourlot et al.

152 2007). We measured the bulk density of the dry soil rewetted at 0.6 m<sup>3</sup>/m<sup>3</sup> of
153 water filled pore space (WFPS) by drying 100 cm<sup>3</sup> of soil (four replicates) at 105°
154 C for three days; it equaled 1.34 and 1.45 g of dry soil per cm<sup>3</sup> for Loam and
155 Silty-loam soils, respectively.

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#### Measurement system

157 The measurement system (Figure 1) was prepared in a climatic chamber and 158 was composed of six measurement lines connected to a vacuum pump that 159 provided airflow to the system. Each line was equipped with the following items: 160 1) a cylindrical glass jar (3200 ml) for soil sample placement, 2) a glass jar 161 collector (1100 ml) for air sampling with a photoacoustic trace gas analyser (P-162 TGA) system (LumaSense Technologies, INNOVA 1412), 3) a flow meter with 163 needle valve for system air flow regulation, and 4) a volumetric air meter to 164 measure total air passed through the line. One line was also equipped with a 165 humidity and temperature data recorder to measure environmental conditions in 166 the volatilization chamber. All parts had air-tight connections through input and 167 output ports, using Teflon or nylon tubes with 4mm internal diameters. Teflon 168 tubes were utilized to avoid NH<sub>3</sub> adsorption in the system.

We determined the air stream NH<sub>3</sub> concentration using the P-TGA. At each measurement, an air sample was collected by the P-TGA's internal pump by manually connecting it to the jar collector with a Teflon tube. The air suction/measurement cycle totalled 79 seconds, of which 38 were for suctioning. The cycle was repeated three to four times until a steady-state NH<sub>3</sub> concentration was attained (Dinuccio *et al.* 2008), which represented the actual concentration of the air stream in the measurement system. The P-TGA's internal pump averaged an air flow rate of 24.7 cm<sup>3</sup>/s so that the total amount of air subtracted to the system for one measurement was 2.82 L. At the end of each measurement, the NH<sub>3</sub> air entering to the volatilization chambers (background) was monitored with the P-TGA and the amount was subtracted from the measured concentration of NH<sub>3</sub>. Under the operating conditions of this experiment, the limit of detection of the P-TGA was 0.2 ppm of NH<sub>3</sub>.

#### 182

#### Ammonia volatilization experiment

183 The experiment was organised on a three randomised complete block 184 design. Six cylindrical glass jars per block (three treatments per two soils) were 185 filled with 1343 and 1451 g of dry soil for Loam and Silty-loam, respectively, to standardize to a final headspace volume of 2000 ml per jar. We attained 0.6  $m^3/m^3$ 186 187 of water-filled pore space (WFPS) by moistening the samples with 295 g and 270 188 g of deionized water to Loam and Silty-loam, respectively. A pin-holed plastic 189 film was used to cover each glass jar and then was placed in a climate-controlled 190 room at 20°C for six days to stabilize the samples prior to experimental start. 191 During this period, the jars were weighed each day; the water content was 192 adjusted when necessary.

The experiment began with jar fertilization. Soil samples were fertilized manually on the jar's surface  $(0.0154 \text{ m}^2)$  at a rate of 90.7 kgN/ha. The fertilization time was different for every treatment and was recorded as a t<sub>0</sub> value for each jar. The measurement then occurred in the same order as for fertilizer application. Immediately after fertilization, the six jars were closed, randomly connected to the lines of the measurement system and the pump was switched on. The flow rate settled at 2 L/min which corresponds to an air renewal rate of one 200 headspace volume per minute in each volatilization chamber (Dinuccio *et al.*201 2008).

The experiment was conducted at 20°C for three different measurement sessions, representing the three blocks, which lasted about 50 hours after fertilization.

A parallel experiment was carried out to evaluate the effect of incorporation on NH<sub>3</sub> volatilization from untreated slurry. In this parallel experiment untreated slurry was manually incorporated into the two soils at the same fertilization rate of the main treatments.

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#### Measurement system evaluation

210 In order to evaluate the reliability of the method with P-TGA, a 211 simultaneous comparison with the acid trap method was carried out. A Drechsel 212 bottle (250 ml), for the containment of the acid trap solution (80 ml of 0.1N 213 H<sub>2</sub>SO<sub>4</sub> solution), was inserted to each line as showed in Figure 1. The comparison 214 between methods was carried out during five intervals of approximately three 215 hours each during which the concentration of NH<sub>3</sub> was measured three nonconsecutive times for each treatment with P-TGA. At the end of each interval, the 216 217 acid solutions contained in the acid traps were collected and the Drechsel bottles 218 accurately washed with deionized water in order to remove all the trapped NH<sub>4</sub><sup>+</sup>-219 N. The Drechsel bottles were then filled with acid trap solution if another interval 220 of measurement was scheduled; otherwise, they were filled with deionized water. 221 The acid traps samples were transferred to volumetric flasks, filled to 250 ml with 222 deionized water and stored at 4°C until the time for NH<sub>4</sub><sup>+</sup>–N content analysis with 223 an ionometer. The amount of NH<sub>3</sub> trapped in acid solution during the

measurement run was determined by a multi-meter equipped with a pH/Ion module and an ammonium selective electrode (ionometer, certified detection limit of 0.1 ppm of  $NH_4^+$ ), and followed the method described by ISO TC 147/6778 (1984).

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#### Data processing and analysis

Photoacoustic TGA-measured data were converted to an actual NH<sub>3</sub>-N emission surface rate by calculating the air flux rate using the elapsed time between the start and end of each measurement interval and their corresponding air volumes.

The emission rates measured for each replication were fitted using a least squares minimization procedure with the derivative of the Michaelis-Menten type equation (Eq. 1) presented by Sommer & Ersbøll (1994) :

236 
$$\frac{dN}{dt} = N_{\text{max}} \frac{k_m}{\left(t + k_m\right)^2} \tag{1}$$

where t is the time from the fertilization event expressed in hour (h), dN / dtis the emission rate expressed in mgNH<sub>3</sub>-N/m<sup>2</sup>/h,  $N_{max}$  is the total loss of NH<sub>3</sub> (mgNH<sub>3</sub>-N/m<sup>2</sup>) as time approaches infinity, and parameter  $k_m$  is the time t when N =  $\frac{1}{2} N_{max}$ . Moreover, parameter  $N_{max}/k_m$  represents the value of the emission rate (mgNH<sub>3</sub>-N/m<sup>2</sup>/h) when t = 0.

The above mentioned parameters were analysed using an ANOVA procedure considering manure and soil as fixed effects, and their interaction and block as random effects.

Emission data have been reported throughout the text as mean value ± standard error of the mean. In order to compare the P-TGA data with the ammonia trapped in the acid solution, total NH<sub>3</sub>-N emitted during each three-hour 248 measurement interval was calculated by integrating the P-TGA data with the fitted 249 equations for the time intervals. A linear regression analysis was carried out to 250 compare these results with the total amount of measured NH<sub>3</sub>-N emitted using 251 acid traps. The analysis was performed using the five measurement interval 252 results, excluding the data below the detection limits of the P-TGA and ionometer 253 (final n = 133).

254

255 **Results** 

256 Measured NH<sub>3</sub>-N emission rates shown in Figure 2 were significantly fitted with the derivative of the Michaelis-Menten equation (average  $R^2 = 0.99$ ). As 257 258 expected, surface-applied treatments showed very high emission rates 259 immediately after fertilization, followed by a strong reduction in a few hours 260 thereafter. In the Michaelis-Menten equation, these results correspond to a high 261 initial emission rate (216.0 mgNH<sub>3</sub>-N/m<sup>2</sup>/h, on average) (Table 3). The low  $k_m$ 262 values also confirmed the quick reduction in emission rates during the first hours 263 (6.3 h, on average).

The ANOVA found the manure effect to not be significant for total N losses while it was significant for total N losses /TAN. Untreated S showed a higher value (0.26 mg/mg) than Untreated S liquid (0.13 mg/mg), while the difference between the Untreated S liquid and the Digested S liquid treatment was not significant. Soil effect was highly significant for both total N losses and total N losses /TAN, showing higher values in Silty-loam than in Loam.

The initial emission rate was highly significant due to the effect of the manure and soil interaction. Specifically, Untreated S showed higher emission

rates in both soils (334.4 mg/NH<sub>3</sub>-N/m<sup>2</sup>/h, on average) *versus* the value for the
liquid fraction of untreated and digested slurry (160.2 and 153.4 mgNH<sub>3</sub>-N/m<sup>2</sup>/h,
respectively), with larger differences in Silty-loam than Loam soil.

275 Incorporating untreated slurry caused very low and constant emission rates 276 throughout the experiment (Figure 2), with a low initial emission rate (7.6 277 mgNH<sub>3</sub>-N/m<sup>2</sup>/h<sup>1</sup>) and a high  $k_m$  value (39.0 h). Incorporated untreated slurry showed a low value of total N losses (308.0 mgNH<sub>3</sub>-N/m<sup>2</sup>, averaged across the 278 279 two soils) (Figure 3), which represents a reduction of 81.7% compared to surface-280 applied slurry. Moreover, when slurry is incorporated, there is a tendency for 281 higher emissions in Loam than in Silty-loam soil, as evidenced by the values of total N losses (537.1 and 79.0 mgNH<sub>3</sub>-N/m<sup>2</sup>, respectively). 282

The linear regression between the P-TGA and the acid traps methods for NH<sub>3</sub>-N emission assessment (Figure 4) was highly significant ( $R^2 = 0.95$ ). However, when using P-TGA, a small underestimation was highlighted by the coefficients (0.925 ± 0.037) and intercept (-4.21 ± 5.72 mgNH<sub>3</sub>/m<sup>2</sup>) of the linear equation.

288

#### 289 Discussion

290 Treat

Treatments comparison

For surface-applied untreated pig slurry, total N losses averaged  $0.26 \pm 0.064$  mg/mg of applied TAN across the two soils. These values were similar to those reported by Sommer & Ersbøll (1994) for field application of pig slurry on harrowed sandy-loam soil. Moreover, the values of total N losses expressed as a percent of TAN are within the range reported by Misselbrook *et al.* (2005) for

field application of pig slurry with low dry-matter (DM) content. The emission
inventory guidebook (Hutchings *et al.* 2009) indicated an emission factor for
spread swine slurry of 0.40 of TAN within a range of 0.20 to 0.80; Reidy *et al.*(2008) reported factors between 0.25 and 0.68.

300 Total N losses/TAN values were  $0.13 \pm 0.064$  for the liquid fraction of pig 301 slurry and  $0.16 \pm 0.064$  for the liquid fraction of digested pig slurry, which 302 suggests that NH<sub>3</sub> emission from land application can be reduced when swine 303 slurry is treated. Generally, it is assumed that a strong, positive relationship 304 between slurry-DM content and volatilization exists (Søgaard et al. 2002; 305 Sommer et al. 2003; Misselbrook et al. 2005) due to the rapid infiltration of 306 diluted slurries into the soil. Solid/liquid separation of both untreated and digested 307 slurry reduces the DM content of the liquid fraction, thereby causing a  $NH_3$ 308 emission reduction after application. The intermediate value of emission for the 309 liquid fraction of digested slurry was probably due to the higher pH of this treated 310 manure that counterbalanced the increased infiltration rate. Previous field studies 311 on NH<sub>3</sub> emissions from land application of anaerobic digested slurries have 312 yielded contrasting results. Rubaek et al. (1996) reported lower emissions with 313 digested rather than with untreated cattle slurry after ryegrass surface application. 314 While not significant, Pain et al. (1990) found a tendency of digested pig slurry to 315 reduce NH<sub>3</sub> emissions compared to undigested slurry on grassland. Specifically, 316 the author reported a total N loss/TAN ratio of 0.21 and 0.13 for undigested and 317 digested slurry, respectively, 48 hours after land application. On the other hand, 318 others (Wulf et al., 2002; Chantigny et al., 2004; Amon et al., 2006) have 319 reported NH<sub>3</sub> emission values in a similar range for different digested slurries as

opposed to untreated slurries. Chantigny *et al.* (2007) concluded that the
discrepancy among studies might be explained by the higher pH of anaerobic
digested slurry which could offset the benefit of improved infiltration.

323 Loam soil showed a lower total N loss than did silty-loam soil for surface-324 applied slurries. This was probably due to its higher sand content that increased 325 the slurry infiltration rate. Whatever process lay behind this difference, it was able 326 to overcome the effect of the higher pH and lower cation-exchange capacity of the 327 Loam versus that of the Silty-loam soil. However, in the instance of the 328 incorporated untreated slurry, we recorded a higher volatilization in Loam than in 329 Silty-loam soil, which might have been caused by the different pH of the two 330 soils. These results underscored the importance of considering soil characteristics 331 and different soil types when evaluating NH<sub>3</sub> emissions from fertilizers.

332 Many cost-effective abatement techniques have been proposed to reduce 333 NH<sub>3</sub> volatilization. Broadcast application and immediate incorporation by plough yields an emission reduction of 80-90% on arable land (Hutchings et al. 2009). 334 335 The average value found in the present experiment (82%) sits within the expected 336 range, even though the amount of NH<sub>3</sub> emitted was estimated in laboratory and 337 the incorporation was performed manually. Moreover, the low values of  $k_m$ 338 estimated for surface-applied manure treatments showed that half of the NH<sub>3</sub> is 339 emitted within six hours after manure spreading; this result points to the 340 importance of implementing regulations on immediate incorporation of manure.

The Michaelis-Menten equation described well the pattern of NH<sub>3</sub>-N
emission rates after manure application. Several authors (Sommer & Ersbøll 1994;
Sogaard *et al.* 2002; Misselbrook *et al.* 2005) used this equation to model

344 accumulated NH<sub>3</sub> losses from field-applied manure, which relates equation 345 parameters to measured variables, such as soil properties, manure properties, and 346 environmental conditions. On the contrary, Sommer et al. (2006) found that the 347 Michaelis-Menten equation could not be fitted to NH<sub>3</sub> emissions from slurry 348 measured in dynamic chambers. Therefore, he concluded that this model was not 349 suitable for laboratory result interpretation. The present experiment gives an 350 operational outcome for the analysis of potential NH<sub>3</sub>-N emissions under constant 351 laboratory conditions and demonstrates the possibility of fitting the results to the 352 Michaelis-Menten equation if NH<sub>3</sub> emission rates are directly measured.

353

#### Measurement system evaluation

354 Our investigations highlighted several benefits associated with the P-TGA 355 method to measure NH<sub>3</sub> volatilization. First, our experiment showed that the 356 combination of a photoacoustic infrared gas analyser with dynamic chambers 357 could make reliable assessments of potential NH<sub>3</sub> emissions when compared to 358 the more utilized acid traps. Second, and different from the latter, direct NH<sub>3</sub> 359 concentration measurement with a P-TGA allows temporal resolution to improve 360 the assessment of  $NH_3$  emission from manures. Specifically, the measurement 361 system allowed performance of high-quality, well-fit analyses, which permitted a 362 good evaluation of the process dynamic. Third, the P-TGA system is less time-363 consuming both during dynamic chamber operations and for sample analyses 364 compared to the acid-traps method. A part of the initial cost of the instrument and 365 scheduled maintenances (once-twice for year), it allows for a drastic reduction in 366 the time and costs of NH4<sup>+</sup> determination. Moreover, the measurement time 367 schedule can be easily tested and modified to better match the NH<sub>3</sub> volatilization

dynamics, so that NH<sub>3</sub> emissions can be determined for a wide range of fertilizer

and soil types.

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  1789-1794.

474 Table 1. Main characteristics of the manures utilized in the experiment.

Type of slurry	pН	$\mathrm{DM}^*$	TOC†	Total N	TAN‡	Total P	Total K
Untreated slurry	8.30	27.8	8.04	3.78	2.91	1.06	2.93
Untreated slurry liquid	8.52	12.6	1.96	2.15	1.99	0.17	3.33
Digested slurry liquid	8.72	13.1	1.96	2.01	1.77	0.13	3.35
Table 2. Main charac	teristics	of the two	o soils util	ized in the	experime	ent.	
Table 2. Main charac	eteristics	of the two	o soils util	ized in the	experime	ent.	

Soil	Sand mg/g	Silt mg/g	Clay mg/g	pH	TOC* mg/g	Total N mg/g	C/N	CEC meq/100g
Silty-loam	158	756	86	6.1	8.4	0.81	10.4	12.5
Loam	484	431	85	8.2	8.3	0.83	10.0	8.2
*TOC: total o	rganic carboi	1						

487 Table 3. Estimated values of the parameters of the Michaelis-Menten equation [dAE/dt 488 =  $N_{max} (k_m/(t+k_m)^2)$ ] and the results of ANOVA for the surface-applied manure 489 treatments.

	Total N losses (N <sub>ma</sub> *)	km	Initial emission rate (N <sub>max</sub> /k <sub>m</sub> )	N <sub>max</sub> /TAN <sup>*</sup>
	mg NH <sub>3</sub> -N/m <sup>2</sup>	h	mg $NH_3$ - $N/m^2$	mg/mg
Manure effect				
Untreated slurry Untreated slurry liquid Digested slurry liquid	1683.2 988.9 1212.2	4.9b 6.1ab 7.8a	334.4 160.2 153.4	0.26a 0.13b 0.16ab
<i>SEM</i> † <i>p(F)</i> ‡ <b>Soil effect</b>	200.36 ns	0.53 0.010	19.4 0.000	0.029 0.027
Silty-loam Loam	1073.7a 749.8b	19.8b 22.1a	139.0 126.0	0.15a 0.12b
$SEM \\ p(F)$	163.6 0.004	0.43 0.000	15.87 ns	0.024 0.004
Manure * Soil				
SEM $p(F)$	188.46 ns	0.39 ns	0.23 0.031	0.027 ns
Block				
p(F)	ns	ns	ns	ns

491 \* TAN: total ammoniacal nitrogen; † SEM: standard error of the mean; ‡p values are reported if p(F) <</li>
 492 0.05



495 Figure 1. Figure 1. Measurement system used in the experiment. Unbroken and dotted496 lines refer to Teflon and nylon tubes, respectively.



515 Figure 2. NH<sub>3</sub>-N emission rates measured with the dynamic chambers combined with 516 photoacoustic infrared gas analyzer for the different fertilizer treatments in Silty-loam

(a) and Loam (b) soils. Continuous lines represent the Michaelis-Menten fitting equation.





Figure 3. Total NH<sub>3</sub>-N losses from untreated slurry surface-applied and incorporated in the two soils utilized in the experiment. Error bars represent the standard error.



530

Figure 4. Linear regression between NH<sub>3</sub> emission estimated by dynamic chambers using acid traps (x) and photoacoustic infrared gas analyzer (P-TGA; y) methods.