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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 (NH₃) 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 NH₃ emissions after application. This study
29 measures potential laboratory NH₃ 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 NH₃ concentration in the air stream.

34 The estimated values of N emitted for surface-applied, untreated pig slurry
35 were 0.26 ± 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 ± 0.064
37 mg/mg and 0.16 ± 0.064 mg/mg, respectively. Initial NH₃-N emission rates from
38 surface-applied, untreated pig slurry were higher than those measured for either
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 NH₃ emissions
44 by 82%.

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

48 temporal resolution that gives a high-quality description of the NH₃ emission
49 dynamic.

50

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

53

54 **Introduction**

55 Animal husbandry and manure management accounts for more than 80% of
56 total ammonia (NH₃) emissions from European agriculture, estimated as 2902 Gg
57 per year; land application of manure, especially slurry, contributes a large
58 proportion of these losses, and represents between 30% and 40% of total
59 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 NH₃ to the atmosphere causes negative effects through
64 acidification and eutrophication of natural ecosystems, as well as via secondary
65 particulate matter formation (Sutton *et al.* 1998; Goebes *et al.* 2003). For these
66 reasons, international and European agreements have established regulations to
67 limit this pollutant, which requires calculating national inventory levels of the
68 contribution from agriculture to total emissions (Erisman *et al.* 1998). These
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 NH₃ 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 NH₄⁺ concentration reduction in the fertilized soil surface
84 from volatilization, infiltration, and nitrification. The pattern of NH₃ 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).

88 Anaerobic digestion, solid/liquid separation of liquid manure, and other
89 manure treatments may also influence gaseous losses because they change the
90 physical and chemical characteristics of manure, and affect the extent of
91 emissions after field spreading (Amon *et al.* 2006; Sommer *et al.* 2006, Petersen
92 & Sørensen 2008). Solid/liquid separation reduces the dry matter in the liquid
93 portion of the slurry, which boosts slurry infiltration. Anaerobic digestion
94 increases TAN content and manure pH, which raises the NH₃ volatilization

95 potential, and decreases dry matter content which increases slurry infiltration rates
96 and decreases NH₃ emissions.

97 The effect of manure and soil properties on NH₃ 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 NH₃ 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 NH₃ 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 NH₄⁺
108 determination), with variable and, in general, low temporal resolution, especially
109 when small NH₃ amounts are emitted. This second drawback leads to information
110 loss, especially during the first hours after fertilizer application when emission
111 rates vary rapidly.

112 Infrared photoacoustic spectroscopy has recently become popular for air
113 sample analysis of several gases (e.g. CO₂, N₂O, CH₄ and NH₃) due to its high
114 accuracy and selectivity (Hoy 1995; Berg *et al.* 2006; Dinuccio *et al.* 2008).
115 Commercial applications of this technology allow automated air sampling, high
116 temporal resolution of measurements, and direct data recording and display of
117 electronic datasets. Mathematical descriptions of the emission dynamics can
118 consequently be performed more adequately. However to-date, few studies exist

119 on the accuracy and reliability of using photoacoustic spectroscopy with dynamic
120 chambers for NH₃ emission assessment.

121 In the present work, we report the results of a laboratory assessment of NH₃
122 emission after soil application of different treated and untreated pig slurry (i.e. no
123 treatment, solid/liquid separation, anaerobic digestion followed by solid/liquid
124 separation) using a system composed of dynamic chambers and a photoacoustic
125 infrared gas analyser. The reliability of this method was evaluated via comparison
126 to the most commonly used acid traps method.

127

128 **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
137 loading rate of 1.35 kg VS/m³/d. The solid and liquid fractions of untreated and
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 $0.6 \text{ m}^3/\text{m}^3$ of
153 water filled pore space (WFPS) by drying 100 cm^3 of soil (four replicates) at 105°
154 C for three days; it equaled 1.34 and 1.45 g of dry soil per cm^3 for Loam and
155 Silty-loam soils, respectively.

156 *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_3 adsorption in the system.

169 We determined the air stream NH_3 concentration using the P-TGA. At each
170 measurement, an air sample was collected by the P-TGA's internal pump by
171 manually connecting it to the jar collector with a Teflon tube. The air
172 suction/measurement cycle totalled 79 seconds, of which 38 were for suctioning.
173 The cycle was repeated three to four times until a steady-state NH_3 concentration
174 was attained (Dinuccio *et al.* 2008), which represented the actual concentration of
175 the air stream in the measurement system. The P-TGA's internal pump averaged

176 an air flow rate of 24.7 cm³/s so that the total amount of air subtracted to the
177 system for one measurement was 2.82 L. At the end of each measurement, the
178 NH₃ air entering to the volatilization chambers (background) was monitored with
179 the P-TGA and the amount was subtracted from the measured concentration of
180 NH₃. Under the operating conditions of this experiment, the limit of detection of
181 the P-TGA was 0.2 ppm of NH₃.

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
186 standardize to a final headspace volume of 2000 ml per jar. We attained 0.6 m³/m³
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.

193 The experiment began with jar fertilization. Soil samples were fertilized
194 manually on the jar's surface (0.0154 m²) at a rate of 90.7 kgN/ha. The
195 fertilization time was different for every treatment and was recorded as a t₀ value
196 for each jar. The measurement then occurred in the same order as for fertilizer
197 application. Immediately after fertilization, the six jars were closed, randomly
198 connected to the lines of the measurement system and the pump was switched on.
199 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).

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

205 A parallel experiment was carried out to evaluate the effect of incorporation
206 on NH₃ volatilization from untreated slurry. In this parallel experiment untreated
207 slurry was manually incorporated into the two soils at the same fertilization rate of
208 the main treatments.

209 *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 H₂SO₄ 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 NH₃ was measured three non-
216 consecutive times for each treatment with P-TGA. At the end of each interval, the
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 NH₄⁺-
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 NH₄⁺-N content analysis with
223 an ionometer. The amount of NH₃ trapped in acid solution during the

224 measurement run was determined by a multi-meter equipped with a pH/Ion
225 module and an ammonium selective electrode (ionometer, certified detection limit
226 of 0.1 ppm of NH_4^+), and followed the method described by ISO TC 147/6778
227 (1984).

228 *Data processing and analysis*

229 Photoacoustic TGA-measured data were converted to an actual $\text{NH}_3\text{-N}$
230 emission surface rate by calculating the air flux rate using the elapsed time
231 between the start and end of each measurement interval and their corresponding
232 air volumes.

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

$$236 \quad \frac{dN}{dt} = N_{\max} \frac{k_m}{(t + k_m)^2} \quad (1)$$

237 where t is the time from the fertilization event expressed in hour (h), dN/dt
238 is the emission rate expressed in $\text{mgNH}_3\text{-N/m}^2/\text{h}$, N_{\max} is the total loss of NH_3
239 ($\text{mgNH}_3\text{-N/m}^2$) as time approaches infinity, and parameter k_m is the time t when N
240 $= 1/2 N_{\max}$. Moreover, parameter N_{\max}/k_m represents the value of the emission rate
241 ($\text{mgNH}_3\text{-N/m}^2/\text{h}$) when $t = 0$.

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

245 Emission data have been reported throughout the text as mean value \pm
246 standard error of the mean. In order to compare the P-TGA data with the ammonia
247 trapped in the acid solution, total $\text{NH}_3\text{-N}$ 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 NH₃-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 NH₃-N emission rates shown in Figure 2 were significantly fitted
257 with the derivative of the Michaelis-Menten equation (average $R^2 = 0.99$). As
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 mgNH₃-N/m²/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).

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

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

272 rates in both soils (334.4 mg/NH₃-N/m²/h, on average) *versus* the value for the
273 liquid fraction of untreated and digested slurry (160.2 and 153.4 mgNH₃-N/m²/h,
274 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 mgNH₃-N/m²/h¹) and a high k_m value (39.0 h). Incorporated untreated slurry
278 showed a low value of total N losses (308.0 mgNH₃-N/m², averaged across the
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
282 total N losses (537.1 and 79.0 mgNH₃-N/m², respectively).

283 The linear regression between the P-TGA and the acid traps methods for
284 NH₃-N emission assessment (Figure 4) was highly significant ($R^2 = 0.95$).
285 However, when using P-TGA, a small underestimation was highlighted by the
286 coefficients (0.925 ± 0.037) and intercept (-4.21 ± 5.72 mgNH₃/m²) of the linear
287 equation.

288

289 **Discussion**

290 *Treatments comparison*

291 For surface-applied untreated pig slurry, total N losses averaged $0.26 \pm$
292 0.064 mg/mg of applied TAN across the two soils. These values were similar to
293 those reported by Sommer & Ersbøll (1994) for field application of pig slurry on
294 harrowed sandy-loam soil. Moreover, the values of total N losses expressed as a
295 percent of TAN are within the range reported by Misselbrook *et al.* (2005) for

296 field application of pig slurry with low dry-matter (DM) content. The emission
297 inventory guidebook (Hutchings *et al.* 2009) indicated an emission factor for
298 spread swine slurry of 0.40 of TAN within a range of 0.20 to 0.80; Reidy *et al.*
299 (2008) reported factors between 0.25 and 0.68.

300 Total N losses/TAN values were 0.13 ± 0.064 for the liquid fraction of pig
301 slurry and 0.16 ± 0.064 for the liquid fraction of digested pig slurry, which
302 suggests that NH₃ 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 NH₃
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 NH₃ 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 NH₃ 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 NH₃ emission values in a similar range for different digested slurries as

320 opposed to untreated slurries. Chantigny *et al.* (2007) concluded that the
321 discrepancy among studies might be explained by the higher pH of anaerobic
322 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 NH₃ emissions from fertilizers.

332 Many cost-effective abatement techniques have been proposed to reduce
333 NH₃ volatilization. Broadcast application and immediate incorporation by plough
334 yields an emission reduction of 80-90% on arable land (Hutchings *et al.* 2009).
335 The average value found in the present experiment (82%) sits within the expected
336 range, even though the amount of NH₃ 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 NH₃ is
339 emitted within six hours after manure spreading; this result points to the
340 importance of implementing regulations on immediate incorporation of manure.

341 The Michaelis-Menten equation described well the pattern of NH₃-N
342 emission rates after manure application. Several authors (Sommer & Ersbøll 1994;
343 Sogaard *et al.* 2002; Misselbrook *et al.* 2005) used this equation to model

344 accumulated NH_3 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_3 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_3 -N emissions under constant
351 laboratory conditions and demonstrates the possibility of fitting the results to the
352 Michaelis-Menten equation if NH_3 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_3 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_3 emissions when compared to
358 the more utilized acid traps. Second, and different from the latter, direct NH_3
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 NH_4^+ determination. Moreover, the measurement time
367 schedule can be easily tested and modified to better match the NH_3 volatilization

368 dynamics, so that NH₃ emissions can be determined for a wide range of fertilizer
369 and soil types.

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- 473

474 Table 1. Main characteristics of the manures utilized in the experiment.
475

Type of slurry	pH	DM*	TOC†	Total N g/kg	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

476 *DM: dry matter; †TOC: total organic carbon; ‡TAN: total ammoniacal nitrogen.
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480 Table 2. Main characteristics of the two soils utilized in the experiment.
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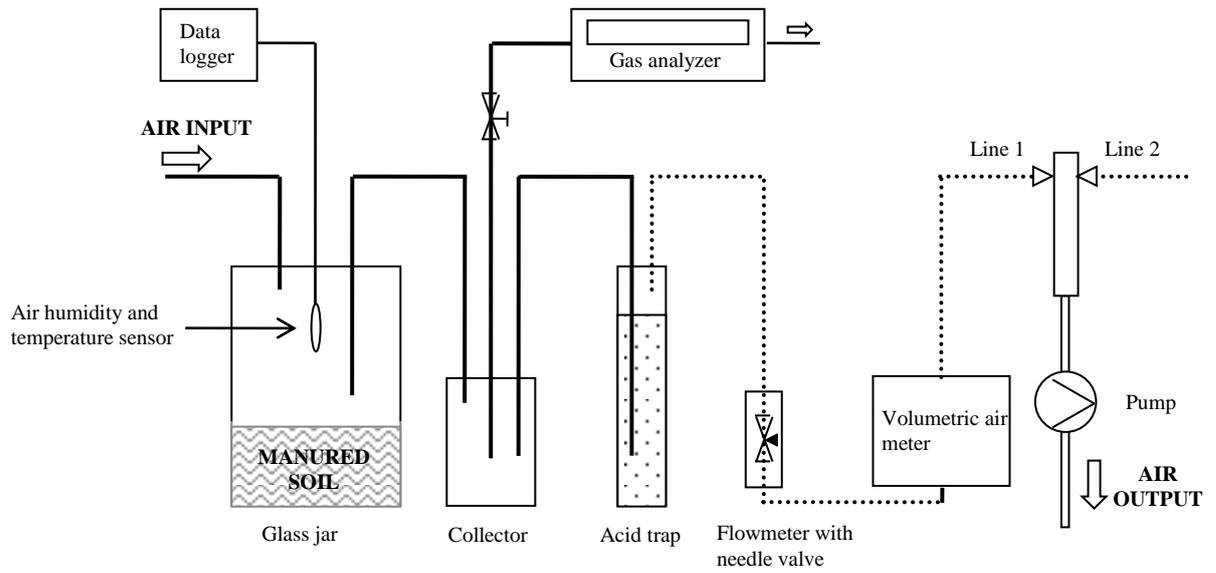
Soil	Sand mg/g	Silt mg/g	Clay mg/g	pH	TOC*	Total N mg/g	C/N	CEC meq/100g
Silty-loam	158	756	86	6.1	8.4	0.81	10.4	12.5
Loam	484	431	85	8.2	8.3	0.83	10.0	8.2

482 *TOC: total organic carbon
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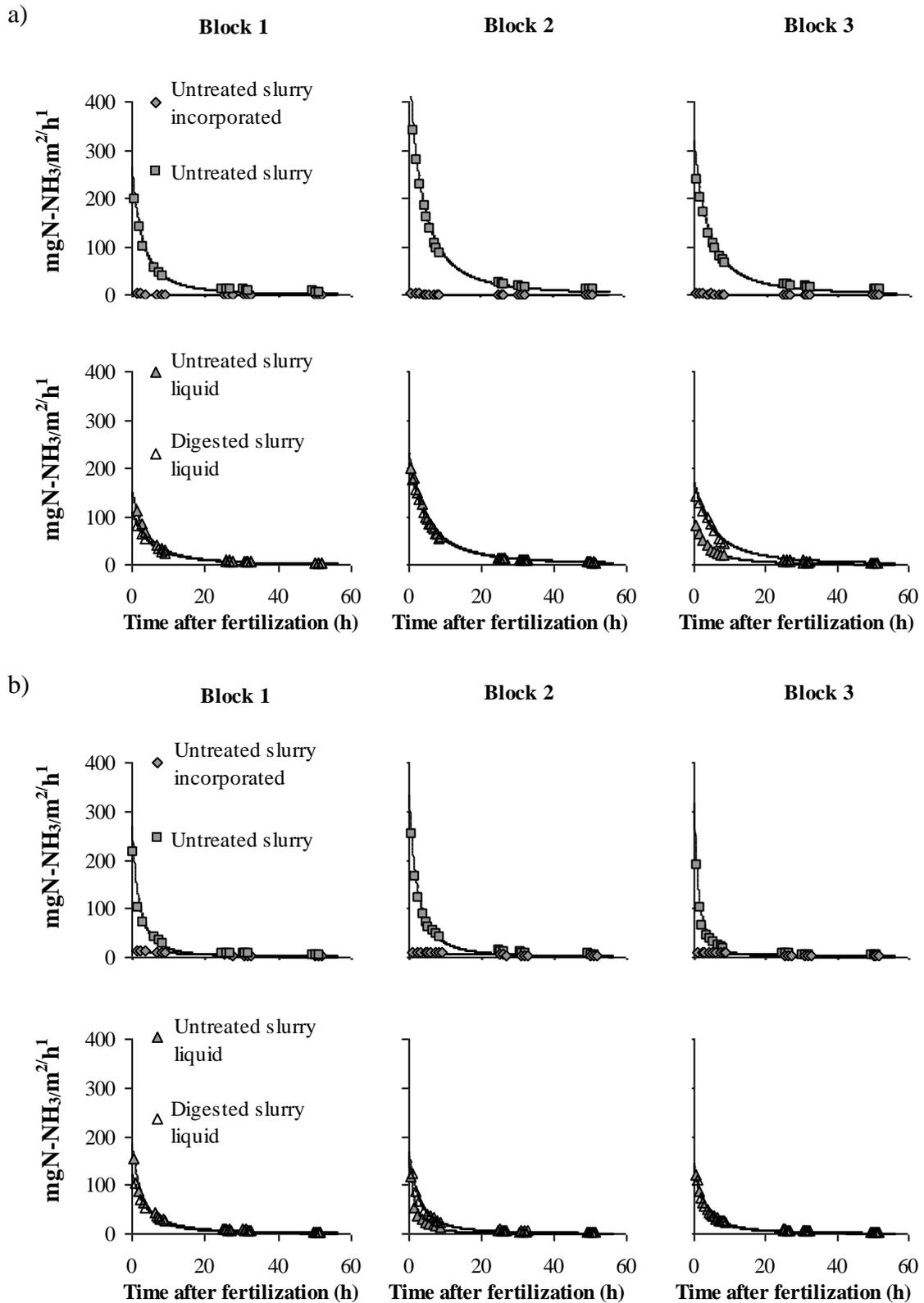
487 Table 3. Estimated values of the parameters of the Michaelis-Menten equation [dAE/dt
488 $= N_{max} (k_m/(t+k_m)^2)$] and the results of ANOVA for the surface-applied manure
489 treatments.
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	Total N losses (N_{max}^*) mg NH_3-N/m^2	k_m h	Initial emission rate (N_{max}/k_m) mg NH_3-N/m^2	N_{max}/TAN^* mg/mg
Manure effect				
Untreated slurry	1683.2	4.9b	334.4	0.26a
Untreated slurry liquid	988.9	6.1ab	160.2	0.13b
Digested slurry liquid	1212.2	7.8a	153.4	0.16ab
SEM†	200.36	0.53	19.4	0.029
$p(F)$ ‡	ns	0.010	0.000	0.027
Soil effect				
Silty-loam	1073.7a	19.8b	139.0	0.15a
Loam	749.8b	22.1a	126.0	0.12b
SEM	163.6	0.43	15.87	0.024
$p(F)$	0.004	0.000	ns	0.004
Manure * Soil				
SEM	188.46	0.39	0.23	0.027
$p(F)$	ns	ns	0.031	ns
Block				
$p(F)$	ns	ns	ns	ns

491 * TAN: total ammoniacal nitrogen; † SEM: standard error of the mean; ‡ p values are reported if $p(F) <$
492 0.05
493



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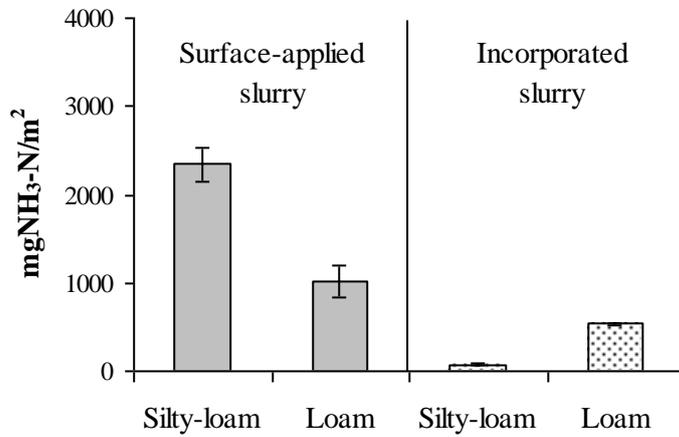


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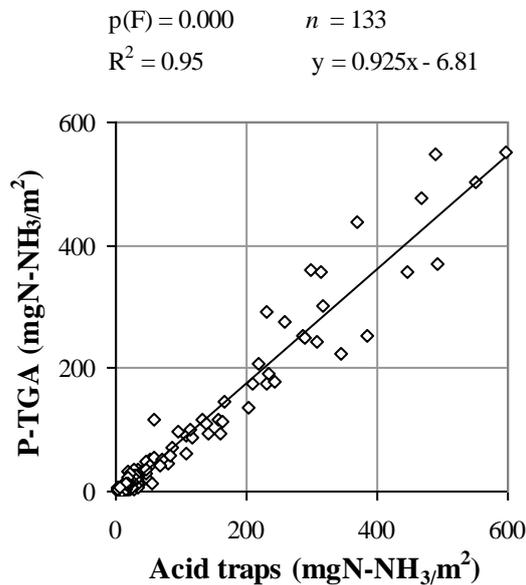
515 Figure 2. $\text{NH}_3\text{-N}$ emission rates measured with the dynamic chambers combined with
 516 photoacoustic infrared gas analyzer for the different fertilizer treatments in Silty-loam

517 (a) and Loam (b) soils. Continuous lines represent the Michaelis-Menten fitting
 518 equation.
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521
 522 Figure 3. Total NH₃-N losses from untreated slurry surface-applied and incorporated in
 523 the two soils utilized in the experiment. Error bars represent the standard error.

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 531 Figure 4. Linear regression between NH₃ emission estimated by dynamic chambers
 532 using acid traps (x) and photoacoustic infrared gas analyzer (P-TGA; y) methods.
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