



Integrated biological treatment of fowl manure for nitrogen recovery and reuse

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ABSTRACT

Biowaste such as animal manure poses an environmental threat, due to among others, uncontrolled emissions of ammonia and additional hazardous gases to the atmosphere. This study presents a quantitative analysis of an alternative biowaste management approach aimed at nitrogen recovery and reduction of contamination risks. The suggested technology combines anaerobic digestion of nitrogen-rich biowaste with biofiltration of the resulting gaseous ammonia. A compost-based biofilter is used to capture the ammonia and convert it to nitrate by nitrifying microorganisms. Nitrogen mass balance was applied to quantify the system's capacity under various fowl manure-loading regimes and ammonia loading rates. The produced nitrate was recovered and its use as liquid fertilizer was evaluated with cucumber plant as a model crop. In addition, emissions of other hazardous gases (N₂O, CH₄ and H₂S) were monitored before and after biofiltration to evaluate the efficiency of the system for treating these gases. It was found that nitrate-rich liquid fertilizer can be continuously produced using the suggested approach, with an over 67 percentage of nitrogen recovery, under an ammonia loading rate of up to 40 g NH₃ per cubic meter biofilter per hour. Complete elimination of NH₃, H₂S, CH₄ and N₂O was achieved, demonstrating the potential of the suggested technology for mitigating emission of these gases from fowl manure. Moreover, the quality of the recovered fertilizer was demonstrated by higher yield performance of cucumber plant compared with control plants treated with a commonly applied organic liquid fertilizer.

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1. Introduction

Management of manure from concentrated animal feeding operations (CAFOs) is a global challenge (De Vries et al., 2012; Pagans et al., 2005). On the one hand, manure can be applied as an alternative source of nutrients in agricultural applications, especially in organic farming where the use of synthetic chemicals is prohibited (Bolado-Rodríguez et al., 2010; Escudero et al., 2012; Wong et al., 1999). On the other hand, manure is a point source pollutant, releasing offensive odors (Hayes et al., 2006) and hazardous gases, including greenhouse gases (GHGs) such as methane (CH₄) and nitrous oxide (N₂O), thus contributing to global warming (Castillo et al., 2012; Clemens and Ahlgrimm, 2001; Monteny et al., 2006; Weiske et al., 2006). CH₄ is produced during anaerobic decomposition of organic material by methanogenic microorganisms

(Nopharatana et al., 1998), while N₂O can be produced during aerobic ammonia oxidation to nitrite (NO₂⁻) and as an intermediate during anaerobic denitrification of nitrate (NO₃⁻) to N₂ (Monteny et al., 2006). Both processes can occur during manure decomposition, depending on the manure nitrogen (N) compounds and content, and oxygen availability (Chadeick et al., 1999; Kroeze, 1994).

Fowl manure (e.g. guano, layers and broilers) is widely used as an alternative source of nutrients in intensive organic farming as it is rich in N, phosphorus (P) and organic matter (OM), and has been reported to have a positive influence on crop production (Butler and Muir, 2006; Giusquiani et al., 1995). A commonly used management practice involves anaerobic digestion of manure with water for several days, in which mineralization of the organic N to ammonia (NH₃) occurs (Hadas et al., 1996; Vymazal, 2007). Following settling, the resulting ammonium-rich supernatant is then supplied to crops at a certain dilution via the irrigation system (fertigation) throughout the growing season (Gross et al., 2008; Hadas et al., 1996). The disadvantages of this practice include possible ammonia toxicity to plants, potential presence of

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pathogens, and clogging of drip-irrigation systems (Gross et al., 2012). In addition, it can significantly contribute to emissions of toxic hydrogen sulfide (H_2S), which are by-products of anaerobic microbial activity (Brunet, 2004; Firer et al., 2008; Lahav et al., 2008; Ni et al., 2010).

Biofiltration has been recognized as a technology to remediate pollutant sources containing gaseous ammonia. Of a variety of organic materials (sludge, peat, coconut fibres, woodchips and more), compost has been reported as a favorable packing material because of its complex microbial communities, good water retention properties, and suitable organic matter content (Chen et al., 2005; Jun and Wenfeng, 2009; Ling and Chen, 2005; Pagans et al., 2005; Smet et al., 2000). Consequently, a procedure for stabilization and utilization of biowaste, specifically conforming with organic farming regulations, was suggested by our group and tested at a laboratory scale (Gross et al., 2012). Briefly, a liquid organic fertilizer production system (LOFPS) was designed, consisting of extraction and nitrification units (EU and NU, respectively). In the EU, N-rich fowl manure is mixed with water and digested for several days. During the digestion process most of the organic N is released as gaseous NH_3 that is forced by air flow into the NU. Since according to the Henderson-Hasselbalch equation a pH-dependent equilibrium exists between ammonia (NH_3) and ammonium (NH_4^+) (pKa of 9.25 at 25 °C), high pH conditions enhance the emission of gaseous ammonia (Berg et al., 2002). Therefore, toward the end of the digestion, pH is raised by adding burnt lime (CaO). Lime application at this stage also contributes to manure sanitization since it allows removal of residual pathogens (Posmanik et al., 2011).

The NU is an aerated biofilter composed of moist mature dairy manure compost (commercially available) which serves both as a biomass carrier and nutritional source, providing a favorable environment for nitrification (Kennens, 1998; Ling and Chen, 2005). The NH_3 coming from the EU passes through a diffuser into the moist compost where it is efficiently dissolved (low Henry constant of 61 M atm⁻¹, Sander, 1999) and mostly converted to NH_4^+ as the pH is buffered by the compost (Chen et al., 2005). Efficient adsorption of NH_4^+ occurs upon the negatively charged surface area of the compost (Smet et al., 2000). After its adsorption the ammonia is converted to nitrate (NO_3^-) by nitrifying microorganisms in a two-step reaction (Jun and Wenfeng, 2009; Yapsakli et al., 2011). Previous studies have demonstrated that nitrifying biofilters are generally dominated by *Nitrosomonas* and *Nitrosospira* spp. as ammonia oxidizers (Jun and Wenfeng, 2009), and by *Nitrobacter* and *Nitrospira* spp. as nitrite oxidizers (Yapsakli et al., 2011). The nitrate is then rinsed out with water and the resulting solution is a nitrate-rich liquid fertilizer (Gross et al., 2012).

In the present study the system was scaled-up and its efficiency in treating high loads of gaseous ammonia and other hazardous gases (H_2S , CH_4 and N_2O) was investigated. Specifically, the aims were to: (i) quantitatively examine the performance of a field-scale system (efficiency of N recovery) under high loading rates of NH_3 emitted from fowl manure extracts; (ii) evaluate the biofilter's potential to prevent emission of hazardous gases (e.g. H_2S , NH_3 , CH_4 and N_2O) that might be produced during manure digestion; (iii) test the quality of the final recovered solution as a nitrogen supplement with a model crop as compared with a commonly applied organic liquid fertilizer.

2. Materials and methods

2.1. Experimental setup

A field-scale LOFPS (Fig. 1) was operated in batch mode for 24 months in an organic farm located in southern Israel. Two 120-L metallic tanks (*Netafim*, Hatzerim, Israel) were used as the EU

into which different quantities of solid fowl manure were introduced at a 1:10 (w/w) manure-to-water ratio (Gross et al., 2008), and digested for 14 days. After 10 days' digestion, to enhance NH_3 volatilization, the slurry pH was raised to about 10 by introduction of 0.1 M CaO solution (Gross et al., 2012) and the digestion was continued for four more days. The manure slurry was mixed by gentle air-jet, maintaining a dissolved oxygen (DO) concentration lower than 1 mg L⁻¹ during the digestion process. The NU was composed of six opaque PVC columns (120 cm long and 15 cm internal diameter) filled with a mixture of 10 L mature dairy manure compost (*Tuff Merom-Golan*, Merom-Golan, Israel) and 10 L plastic beads (diameter of 10 mm, *Aridal bio-balls*, Kefar Hasidim, Israel). Densities of the compost and plastic beads were 250 and 160 kg m⁻³, respectively. Initial pH and electric conductivity (EC) of the compost material were 8.1 and 0.2 dS m⁻¹, respectively. Initial N_{total} in the compost material was 1.8%, while total ammonia nitrogen (TAN) and NO_3^- -N were 120 and 70 mg kg⁻¹, respectively. The same matrix was used throughout the study. No nitrifying culture was inoculated into the matrix and the biological process relied on the natural microbial population in the compost. The exhaust gas from the EU was introduced into the NU column through a perforated plate that was located underneath the filter-bed, allowing homogeneous gas flow. The gas was released at the column's top passing through a 4% boric acid ammonia trap (Fig. 1). The filter-bed of each column was watered daily at a rate of 1 L day⁻¹ by regulated drip-irrigation (1 L h⁻¹) to ensure that the compost media remained moist (40–50% water content, w/w). The gas flow rate from the EU to NU was measured and controlled by a set of flow meters (*Emproco*, Ashkelon, Israel), ensuring a permanent flow rate of 5 L min⁻¹. To reduce high concentrations of NH_3 and maintain the aeration in the NU, the exhaust gas from the EU was diluted (prior to the NU inlet) with a 15 L min⁻¹ of atmospheric (ammonia-free) air by the blower (Fig. 1). At the end of each experiment, the EU was emptied and was ready for a new batch. To quantify the LOFPS capacity at different manure-loading rates, increasing amounts of manure were digested in the EU.

2.2. Chemical analyses

Manure slurry samples (15 mL) were taken from the EU every two days during the digestion process and analyzed for pH, oxidation reduction potential (ORP), EC and DO (*WTW*, Multimeter, 420i, Weilheim, Germany). For N analyses, samples were centrifuged for 3 min at 1075 g (*Multifuge 1* Heraeus centrifuge) and the supernatant was separated from the solid phase and analyzed for total N (N_{total}) and total ammonia N (TAN = NH_3 -N + NH_4^+ -N). Solids were dried at 65 °C for 96 h, extracted in 1 M KCl at a 1:5 (solid to liquid) ratio and the liquid and solid extracts were analyzed by Kjeldhal for N_{total} and TAN following the distillation procedure (APHA, 2005; Soil and Plant Analysis Council, 1999). The fertilizer (washout from the NU on day 14) was analyzed for N_{total} by persulfate method, TAN by Nesslerization method, NO_2^- by diazo color method, and NO_3^- by second-derivative method (APHA, 1989, 2005). Organic N (N_{org}) was calculated as the difference between N_{total} and inorganic N forms (TAN + NO_2^- + NO_3^-). In addition, exhaust gas from the NU was passed through a 4% boric acid trap and the acid was analyzed daily for NH_4^+ by the Nesslerization method. To complete the N mass balance, samples of raw manure from the EU and compost from the NU were routinely analyzed for N forms (TAN, NO_2^- and NO_3^-).

2.3. Gaseous emissions

Gas samples from the headspace of the EU and from the flow cell at the top of the NU (Fig. 1) were withdrawn daily into 1-L sample

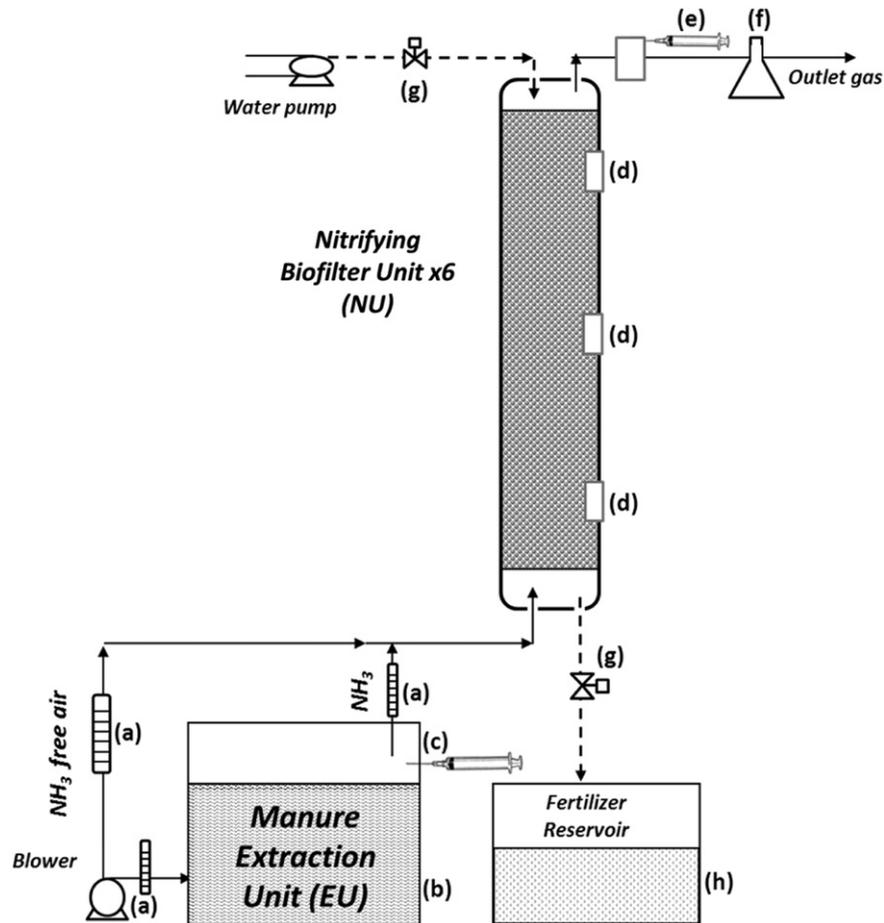


Fig. 1. Schematic drawing of the field-scale liquid organic fertilizer production system (LOFPS): (a) flow meter and controller; (b) manure extract; (c) headspace gas sampler; (d) compost sampling port; (e) flow cell for gas sampling; (f) ammonia trap; (g) normally closed water valve; (h) leachate sampling port. In practice, 6 NU columns were used in parallel.

bags (ProFlexFilm, SKC, Eighty four, PA) sealed with polypropylene valve and septum. Gas samples were analyzed for N_2O and CH_4 using a CP-3800 gas chromatograph (Varian, Walnut Creek, CA) with a $0.53 \text{ mm} \times 30 \text{ m Rt-Q-Bond}$ column (Restec, Bellefonte, PA). N_2O was measured using an electron capture detector with He as the carrier gas (10 mL min^{-1}) and N_2 as the makeup gas (20 mL min^{-1}). Temperatures of the injector, column, and detector were 220, 40, and $300 \text{ }^\circ\text{C}$, respectively. CH_4 was analyzed with a thermal conductivity detector using He as the carrier gas (7 mL min^{-1}). Temperatures of the injector, column, and detector were 225, 30, and $225 \text{ }^\circ\text{C}$, respectively. To estimate H_2S emission, gas from the EU and NU were introduced into a 10% zinc-acetate trap (Firer et al., 2008) and samples were analyzed daily by iodometric method (APHA, 2005).

2.4. Evaluation of fertilizer quality

Together with N-form characterization (Section 2.2), fertilizer quality was further evaluated by analysis of total P (P_{total}) and potassium (K) by Varian 280 ICP analyzer (APHA, 2005). In addition, fertilizer performance was tested in a fertilization study. As the process does not breach any rule of the organic farming regulation (IFOAM, 2005) the LOFPS fertilizer was compared with an organic NuGro 6-2-4 liquid fertilizer (Natural Products, UK) which is commonly used by organic farmers in Israel. Cucumber plants (*Cucumis sativus*) were used as the model crop due to their short growing season (~ 60 days) and because their yield is highly influenced by N, P, and K (Wang et al., 2008). Cucumber seedlings ($n = 72$) were

planted in 10-L plastic pots filled with planting soil (tuff and peat mixture 1:1, v/v). Pots were placed in a greenhouse in a randomized-block design, where the temperature ranged between 20 and $30 \text{ }^\circ\text{C}$. Plants were automatically drip-irrigated for 1 h daily by a computerized system at a flow rate of 1 L h^{-1} (i.e. 1 L day^{-1}). To ensure similar N application in both fertilization treatments, fertilizer subsamples were routinely analyzed for N_{total} and the dose was calculated accordingly. Plants were fertigated during the experiment with an average N_{total} concentration of 80 mg L^{-1} for a period of 60 days between March and May 2009. Unfertilized plants grown under the same conditions served as negative control. Plant shoot height was monitored periodically and at the end of the experiment, cucumber fruits were picked and weighed in five sessions to evaluate crop production.

2.5. Statistical analysis

The effects of the different manure-loading regimes as well as fertilization regimes on the system's efficiencies and cucumber growth performance were statistically analyzed by one-way ANOVA. When differences were significant, a post hoc test was used.

3. Results and discussion

3.1. Manure extraction

Mineralization of N_{org} to ammonia (ammonification) started shortly after initiation of the experiment (Fig. 2a) and reached

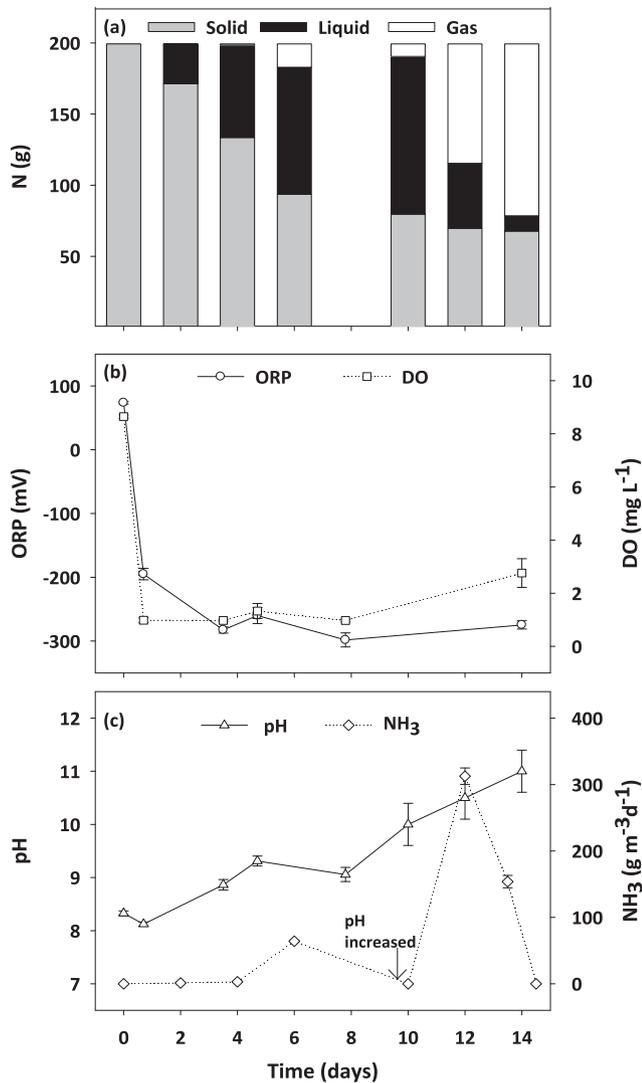


Fig. 2. Extraction efficiency during 14-days digestion of fowl manure: (a) dynamics of nitrogen forms in the digestion tank: solid = manure organic N; liquid = dissolved ammonia N in extract; and gas = NH₃ in exhaust gas; (b) concentration of dissolved oxygen (DO) and oxidation reduction potential (ORP) over time; (c) pH in manure slurry and daily NH₃ concentration in the exhaust gas. Values are based on three replicates \pm SE.

about 70% after 10 days in all digestions, regardless of the total manure weight introduced (Table 1). Despite the air-jet used for mixing, reducing conditions and low oxygen concentration were maintained throughout the manure digestion (Fig. 2b), which minimized ammonia oxidation activity (Gross et al., 2008; Kelleher et al., 2002). The reducing conditions were maintained as a result of high oxygen demand of the slurry. The initial pH value of the

manure slurry was 8.2 ± 0.05 ; during the first nine days, due to ammonification of organic N, it increased gradually to ~ 9 (Fig. 2c). On day 10, the pH was raised to ~ 10 with the addition of CaO. This increased the NH₃ concentration in the exhaust gas, which consequently increased the NH₃ loading rate into the NU (Fig. 2c). On day 10, the NH₃ loading rate rose sharply to over $313 \text{ g m}^{-3} \text{ biofilter day}^{-1}$ followed by a gradual decrease, back to zero, toward day 14 (Fig. 2c). Overall, over 90% of the ammonified N_{org} was emitted from the EU to the NU (Fig. 2a). In other words, the remaining slurry contained mainly N_{org} which accounted for about 30% of the initial manure N. These findings are in agreement with other fowl manure digestion studies (Gross et al., 2008, 2012). The CaO added toward the end of the digestion process sanitized the biosolids (Posmanik et al., 2011). The slight increase in DO on day 14 indicates a reduction in microbial activity and possibly in OM concentration (Fig. 2b).

Several studies have demonstrated that application of treated biosolids improve soil fertility and stimulate N cycling processes in soil as they may contain organic carbon, N, P and K compounds (Kelly et al., 2011; Speir et al., 2004). It should be noted that the residual manure from the EU (after lime treatment) despite its high pH (>10) can be utilized as a soil amendment while meeting Europe's strict 'low-risk biowaste' regulations (Posmanik et al., 2011). Yet, other studies suggest that long-term land application of treated manure might negatively impact soil properties, fertility and microbial diversity including N transforming microorganisms (Arthurson, 2009; Garcia-Gil et al., 2004; Lawlor et al., 2000). Therefore, the effect of land application of digested manure on N₂O emission should be investigated, however this is beyond the scope of this study.

3.2. Ammonia biofiltration

The capacity of the NU biofilter to adsorb ammonia and convert it to NO₃⁻ was evaluated under different NH₃ loading rates (i.e. different manure loads in the EU) as summarized by representative N mass balances (Table 1). For all manure loads, the NU captured between 92% of the emitted NH₃ at the highest load ($4215 \text{ g N m}^{-3} \text{ biofilter}$) and 100% at the lowest ($856 \text{ g N m}^{-3} \text{ biofilter}$), demonstrating its significantly higher efficiency under the lower load ($p < 0.05$, Table 1). N losses at the highest manure loads (8% of the emitted NH₃ from manure) were mainly a result of NH₃ volatilization, trapped by the boric acid (Table 1). In spite of the high NH₃ adsorption at all loading rates, the biological N transformations in the NU were highly affected by NH₃ loads. At the lowest manure load, virtually all of the TAN was oxidized to NO₃⁻ and recovered in the fertilizer. However, at the mid and higher loading rates, less TAN was oxidized to NO₃⁻. Overall, 67% of the total manure N was recovered in the fertilizer under lower manure load, followed by 45% and 23% under mid and higher loads, respectively.

A compilation of results from several studies using compost biofilters to treat NH₃ suggests a similar pattern. For example, Jun and Wenfeng (2009) reported 100% removal efficiencies of low ($0.02\text{--}0.1 \text{ g m}^{-3}$) NH₃ concentration from contaminated air,

Table 1

Nitrogen mass balance in the LOFPS for three representative ammonia loading regimes (low, medium, and high). All values are normalized to biofilter volume unit (m³). Values are the average of four replicates \pm SE. Different capital letters indicate significant differences between treatments ($p < 0.05$).

Loading regime	Manure N/biofilter unit (g m ⁻³)	Residual N in manure (EU) (g m ⁻³)	N released from manure (g m ⁻³)	Residual N in biofilter (NU) (g m ⁻³)	Recovered N in fertilizer (g m ⁻³)	Lost NH ₃ -N ^a (g m ⁻³)	NH ₃ removal efficiency ^b (%)	Total recovery efficiency ^c (%)
Low	856.2 ± 42.1	273.2 ± 16.2	583 ± 36.7	10.1 ± 4.7	572.9 ± 41.2	Not detected	100 ± 0^A	66.7 ± 2.2^A
Medium	1288.5 ± 26.2	409.2 ± 33.0	879.3 ± 26.4	271.9 ± 31.5	580.3 ± 30.2	27.1 ± 9.4	96.9 ± 1.1^{AB}	44.9 ± 1.7^B
High	4215 ± 67.4	1264.5 ± 20.2	2950 ± 47.2	1757.1 ± 28.8	955.9 ± 90.6	237.5 ± 16.1	91.9 ± 0.6^B	22.6 ± 1.8^C

^a Losses of N from the system, as monitored by NH₃ trap.

^b Calculated according to the ratio of recovered and residual N in the NU to N released from the manure.

^c Calculated according to the ratio of recovered N in the fertilizer to initial manure N.

whereas Pagans et al. (2005) reported only 47% removal efficiency for the treatment of exhaust gases from animal biowaste, with a NH_3 loading rate of $37 \text{ g m}^{-3} \text{ biofilter h}^{-1}$. The capacity of the NU for NH_3 treatment was significantly higher than in these previous reports. Whereas in the other reports the aim was NH_3 removal, in the current study an attempt was made to convert the emitted NH_3 to NO_3^- for recovery and reuse. The balance between three dominant processes in the NU is likely to be the reason behind the improved biofiltration capacity. First, gaseous NH_3 reacts with H_2O to form NH_4^+ and OH^- as follows: $\text{NH}_3(\text{g}) + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+(\text{aq}) + \text{OH}^-$ (Berg et al., 2002). The NH_4^+ is then adsorbed onto the negatively charged compost surface and the solution pH rises. If not treated, the pH continues to increase and more of the TAN is in the form of gaseous NH_3 , resulting in losses from the biofilter. However, if it is converted to NO_3^- as in the LOFPS, pH is reduced during the process as follows: $\text{NH}_4^+ + 1.5\text{O}_2 \rightarrow \text{NO}_2^- + 2\text{H}^+ + \text{H}_2\text{O}$ (Metcalf and Eddy Inc., 2003). This in turn frees sorption sites on the filter-bed and shifts the equilibrium toward NH_4^+ , which can be further adsorbed. Finally, by rinsing the biofilter (for NO_3^- recovery), its salinity is reduced, eliminating any negative feedback on the biological activity (Ye et al., 2009). These three processes (ammonia adsorption, nitrification and rinsing), balanced the pH in the NU compartment which ranged between 6.6 and 8.3, resulting in a high biofiltration capacity. It should be noted that since 2 mol of acidity (H^+) are produced for each mole of alkalinity (OH^-), the biofilter's pH is expected to drop. Both the frequent biofilter washes (when NO_3^- is recovered) and the compost buffer capacity intensify this process. Staggered introduction of new compost to the biofilter would further mitigate this expected pH drop.

Fig. 3 summarizes the results of 27 experiments with different NH_3 loading rates, demonstrating a negative correlation between NH_3 loading rate into the NU and N recovery in the fertilizer. When NH_3 loading rates were lower than $40 \text{ g NH}_3 \text{ m}^{-3} \text{ biofilter h}^{-1}$, over 95% of the N was recovered (mainly as NO_3^-) in the fertilizer, but this decreased exponentially to about 40% or less as the rates surpassed $80 \text{ g NH}_3 \text{ m}^{-3} \text{ biofilter h}^{-1}$. The sharp drop in NO_3^- recovery is mainly attributed to the negative toxic effect of NH_3 and possibly other gases (e.g. H_2S) on the nitrification rate, which is a multistep biological process. For example, in a 40–50% moisture compost biofilter, the suggested loading threshold of $40 \text{ g NH}_3 \text{ m}^{-3} \text{ biofilter h}^{-1}$ corresponded to a dissolved TAN concentration of 320–400 mg L^{-1} . Taking into account the pH in the filter-bed which ranged between 6.6 and 8.3, and the average nitrification rate (data

not shown), the NH_3 concentration in the filter-bed was calculated to range between 5 and 15 mg L^{-1} . These concentrations did not seem to inhibit biological activity. However, at the higher loading rates, the pH in the filter-bed ranged between 8 and 8.4, resulting in NH_3 concentrations between 20 and 80 mg L^{-1} . These concentrations have been reported to have a negative effect on the activity of ammonia-oxidizing bacteria and nitrite-oxidizing bacteria (Féray and Montuelle, 2002; Kim et al., 2006; Welander et al., 1998; Yun and Kim, 2003) and would therefore explain the fast decline in the efficiency of nitrification in treating higher concentrations of NH_3 . In summary, optimization of the LOFPS' capacity to treat NH_3 is dependent on the balance between NH_3 emission from the EU (i.e. manure-loading) and its oxidation in the NU.

3.3. Gaseous emissions

3.3.1. Nitrous oxide emissions

One of the major challenges in animal manure management is mitigation of N_2O emitted during treatment of manure (Clemens and Ahlgrimm, 2001; Monteny et al., 2006; Weiske et al., 2006). N_2O emissions from the manure extract (EU) were highest on the first day of extraction with an average of 21 $\text{mg kg}^{-1} \text{ manure h}^{-1}$ (equivalent to 22 ppmv). The emission thereafter (days 2–10) dropped to an average $0.9 \pm 0.1 \text{ mg kg}^{-1} \text{ manure h}^{-1}$ (equivalent to about $0.92 \pm 0.14 \text{ ppmv}$) (Fig. 4a). The major pathway for the formation of N_2O is the reduction of NO_3^- or NO_2^- (Monteny et al., 2006). Thus, the conditions of low DO and negative ORP during digestion (Fig. 2b) and up to 1800 $\text{mg NO}_3^- \text{ kg}^{-1}$ as $\text{NO}_3^- \text{ N}$ in the manure (Posmanik et al., 2011) were favorable for denitrification and N_2O production on the first day of extraction. Once the NO_3^- concentration decreased (after two days), the concentration of N_2O

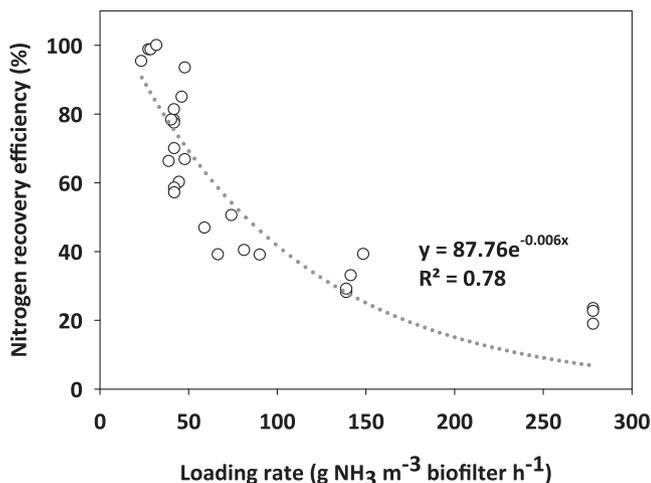


Fig. 3. Gaseous ammonia recovery efficiency of the nitrification biofilter unit (NU) as a function of ammonia loading rate. "Efficiency" was defined as: N recovered from the NU (fertilizer N/volatilized $\text{NH}_3\text{-N}$ from the EU $\times 100$).

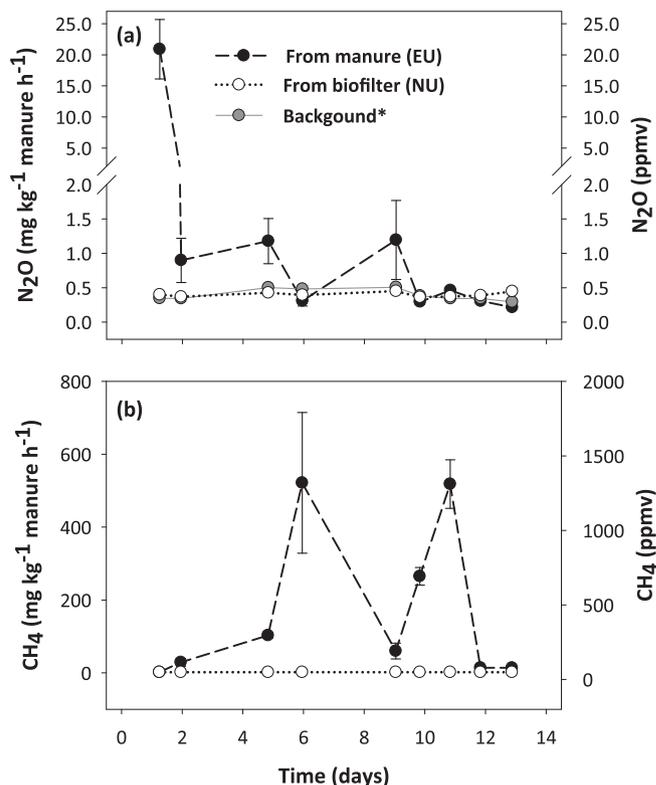


Fig. 4. N_2O (a) and CH_4 (b) emission loads during manure extraction and after biofiltration as monitored during 14 days of processing. On the left axis, values are normalized to the mass of manure in the EU. On the right axis, the values are expressed volumetrically. Results are based on three replicates $\pm \text{SE}$. *No background levels of CH_4 were found (detection limit, 3 ppmv).

decreased to almost atmospheric background (Fig. 4a). The slightly higher N_2O emission on days 2–10 might be explained by partial nitrification in the slurry resulting from air-jet mixing in the EU coupled with denitrification (Bernet and Béline, 2009). It should be noted that the exhaust gas from the EU was diluted ($\times 4$) before entering the NU with atmospheric air, containing background concentration of 0.39 ppmv, suggesting an actual inlet concentration ranging between 0.3 and 7 ppmv. Interestingly, at all times the exhaust N_2O from the NU was not higher than the background concentration, demonstrating the biofilter efficiency in removing N_2O . It is assumed that N_2O dissolves in the NU liquid phase (Kunert, 1922) and is reduced to N_2 by denitrifying bacteria in anaerobic niches within the NU (Monteny et al., 2006). However, the specific N_2O -retention mechanism in the NU biofilter is still unclear and should be further investigated.

3.3.2. Methane and hydrogen sulfide emission

Emission of CH_4 was recorded from the EU but not from the NU. CH_4 concentration was low, ranging between 10 and 100 $mg\ kg^{-1}$ manure h^{-1} except on days 5 and 10 when it was somewhat higher, about 500 $mg\ kg^{-1}$ manure h^{-1} (Fig. 4b). Taking into consideration the dilution ($\times 4$), the inlet concentration of CH_4 into the NU ranged between 8 and 350 ppmv, while no CH_4 was detected in the NU exhaust gas. Interestingly, there was no evidence of H_2S emission from the manure extracts (EU) or from the NU biofilter despite of being a favored electron acceptor. Sulfate (SO_4^{2-}) reduction via assimilatory or dissimilatory pathways by sulfate-reducing bacteria is known to be a major source of H_2S emission from animal manure (Mackie et al., 1998). Moreover, similar fowl manure digestion without the air-jet mixing resulted in emission of H_2S (data not shown). It is therefore assumed that there was probably some sulfate reduction, but since H_2S can be easily oxidized or rapidly precipitated as metal sulfides, or both, it was not detected (Ulrich et al., 1997).

The lack of significant CH_4 and H_2S emissions from the manure extract despite the reducing conditions (Fig. 2b) was attributed in the first days partly to the initial presence of NO_3^- and NO_2^- , which are preferred electron acceptors in terms of anaerobic respiration (Gerardi, 2003). A high concentration of NH_3 , high pH and slight introduction of oxygen from the air-jet mixing were factors affecting this lack of emissions during later stages of digestion (Fig. 2c) (Chen et al., 2008; Kelleher et al., 2002). Among the environmental parameters measured in the EU (e.g. pH, temperature, ORP), the C:N ratio was noticeably low, ranging from 0.7 to 5.1, which is considered out of range for efficient methanogenesis (Marchaim, 1992; Mirzoyan et al., 2008).

3.4. Reuse of recovered nitrate

To examine the potential of the NO_3^- -rich solution produced by the LOFPS as a nitrogen supplement, it was used in a plant growth

Table 2

Chemical characteristics of the LOFPS-based and *NuGro* fertilizers. Values are the average of three replicates.

Parameter	Concentration in fertilizer ($mg\ L^{-1} \pm SE$)	
	<i>NuGro</i>	LOFPS
Total nitrogen (N_{total})	52,900 \pm 2471	9173 \pm 180
Total ammonia N (TAN)	23,066 \pm 1196	3207 \pm 78
Nitrate N (NO_3^- -N)	514 \pm 37	5692 \pm 65
Nitrite N (NO_2^- -N)	N.D. ^a	257 \pm 17
Organic N (N_{org})	29,320 \pm 1238	N.D. ^a
Total phosphorus (P_{total})	20,000 ^b	0.3 \pm 0.02
Potassium (K)	40,000 ^b	50 \pm 4

^a N.D. not detected.

^b According to manufacturer's specifications.

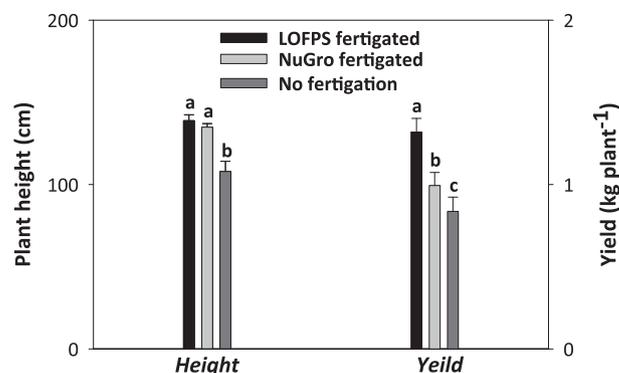


Fig. 5. Growth (height) and yield (fruit weight) performance of cucumber plants fertigated with *NuGro*, LOFPS-based fertilizer and control for 60 days. Values are the average of 24 replicates \pm SE. The letters indicate statistical significance ($p < 0.05$) between treatments.

bioassay. As the process does not breach any rule in the organic farming regulation (IFOAM, 2005) the NO_3^- rich fertilizer can be considered for use in organic farming. Thus, it was compared to the performance of the widely used organic liquid fertilizer (*NuGro*). The chemical properties of the LOFPS and *NuGro* fertilizers are summarized in Table 2. N was the dominant macronutrient in the solution recovered from the LOFPS, at approximately 9.2 $g\ N\ L^{-1}$, and a NO_3^- -N:TAN ratio of 1.8. The NO_2^- content was lower than 3% of the N_{total} and therefore negligible in terms of final application (i.e. after dilution with irrigation water). The *NuGro* fertilizer contained mostly N_{org} and TAN (55% and 44% of N_{total} , respectively), undetectable levels of NO_2^- , and a significantly lower concentration of NO_3^- (0.05% of N_{total}) than the LOFPS fertilizer. The concentrations of P_{total} and K in the LOFPS fertilizer were significantly lower than in the *NuGro* fertilizer and originated from the biofilter media and the wash water used in the preparation process (i.e. not from the manure).

Growth (plant height) and yield (fruit weight) of cucumber plants that were fertilized by the LOFPS and *NuGro* fertilizers as compared to negative control are summarized in Fig. 5. The final height of the plant shoots was similar for both fertigation treatments and as expected significantly higher than the negative control ($p < 0.05$). However, the LOFPS fertilizer-treated plants gave an average 25% and 37% higher yield than the *NuGro*-treated plants and the untreated plants, respectively ($p < 0.05$). This advantage of the LOFPS fertilizer may be attributed to the use of a combination of NO_3^- -N and TAN, whereas TAN is the sole N form in *NuGro*. These results agree with previous reports indicating lower yields following the use of an ammonia-based organic fertilization regime such as guano extracts (Bar-Tal et al., 2004; Ho and White, 2005; Navarro et al., 2005).

The findings of the current research may help to design a full scale system for the treatment of animal biowaste. Final application of the suggested approach may bring mutual benefit, both as a biowaste management procedure and as an alternative source for nutrients for plant growth. The economic feasibility of the suggested technology, together with further investigation regarding its energy and water balances should be addressed in future studies.

4. Summary and conclusions

A scheme for biowaste management, biofiltration of NH_3 and production of NO_3^- -rich organic fertilizer was quantitatively analyzed for its capacity to mitigate NH_3 emissions while reusing the biowaste N. High recovery ($>67\%$) of N from fowl manure as NO_3^- -rich liquid fertilizer was demonstrated with virtually complete

recovery of NH_3 up to $40 \text{ g NH}_3 \text{ m}^{-3} \text{ biofilter h}^{-1}$. In addition, cucumber plants fertigated with the LOFPS NO_3^- -rich fertilizer exhibited 25% higher yields than plants fertigated with *NuGro*. In a separate publication, we showed that the residual manure sludge can be safely utilized, with beneficial agricultural properties (Posmanik et al., 2011), and therefore overall, complete recovery and reuse of N was established. Moreover, complete elimination of NH_3 , H_2S , CH_4 and N_2O emissions was achieved, demonstrating the robustness of the LOFPS as a N-rich biowaste management scheme in general, and as a source of high-quality N fertilizer for use in organic agriculture in particular.

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References

- APHA, AWWA, WEF, 2005. Standard Methods for the Examination of Water and Wastewater, 21st ed. American Public Health Association, Washington, DC.
- APHA, AWWA, WPCF, 1989. Standard Methods for the Examination of Water and Wastewater, 17th ed. American Public Health Association, Washington, DC.
- Arthurson, V., 2009. Closing the global energy and nutrient cycles through application of biogas residue to agricultural land – potential benefits and drawback. *Energies* 2, 226–242.
- Bar-Tal, A., Yermiyahu, U., Beraud, J., Keinan, M., Rosenberg, R., Zohar, D., Rosen, V., Fine, P., 2004. Nitrogen, phosphorus, and potassium uptake by wheat and their distribution in soil following successive, annual compost applications. *J. Environ. Qual.* 33, 1855–1865.
- Berg, J.M., Tymoczko, J.L., Stryer, L., 2002. *Biochemistry*, fifth ed. W.H. Freeman and Company, New York.
- Bernet, N., Béline, F., 2009. Challenges and innovations on biological treatment of livestock effluents. *Bioresour. Technol.* 100, 5431–5436.
- Bolado-Rodríguez, S., García-Sinovas, D., Alvarez-Benedí, J., 2010. Application of pig slurry to soils. Effect of air stripping treatment on nitrogen and TOC leaching. *J. Environ. Manage.* 91, 2594–2598.
- Brunet, L., 2004. Hazardous Gases: Fact Sheet of Ministry of Agriculture. Food and Rural Affairs, Ontario, CA.
- Butler, T.J., Muir, J.P., 2006. Dairy manure compost improves soil and increases tall wheatgrass yield. *Agron. J.* 98, 1090–1096.
- Castillo, S., Mac-Beath, I., Mejía, I., Camposeco, R., Bazan, G., Morán-Pineda, M., Carrera, R., Gómez, R., 2012. Role of average speed in N–O exhaust emissions as greenhouse gas in a huge urban zone (MVMZ): would we need a cold sun? *J. Environ. Manage.* 98, 56–64.
- Chadeick, D., Sneath, R., Phillips, V., Pain, B., 1999. A UK inventory of nitrous oxide emissions from farmed livestock. *Atmos. Environ.* 33, 3345–3354.
- Chen, Y.X., Yin, J., Wang, K.X., 2005. Long-term operation of biofilters for biological removal of ammonia. *Chemosphere* 58, 1023–1030.
- Chen, Y., Cheng, J.J., Creamer, K.S., 2008. Inhibition of anaerobic digestion process: a review. *Bioresour. Technol.* 99, 4044–4064.
- Clemens, J., Ahlgrimm, H.-J., 2001. Greenhouse gases from animal husbandry: mitigation options. *Nutr. Cycl. Agroecosyst.* 60, 287–300.
- De Vries, J.W., Groenestein, C.M., De Boer, I.J.M., 2012. Environmental consequences of processing manure to produce mineral fertilizer and bio-energy. *J. Environ. Manage.* 102, 173–183.
- Escudero, A., González-Arias, A., Del Hierro, O., Pinto, M., Gartzia-Bengoetxea, N., 2012. Nitrogen dynamics in soil amended with manures composted in dynamic and static systems. *J. Environ. Manage.* 108, 66–72.
- Féray, C., Montuelle, B., 2002. Competition between two nitrite-oxidizing bacterial populations: a model for studying the impact of wastewater treatment plant discharge on nitrification in sediment. *FEMS Microbiol. Ecol.* 42, 15–23.
- Firer, D., Friedler, E., Lahav, O., 2008. Control of sulfide in sewer systems by dosage of iron salts: comparison between theoretical and experimental results, and practical implications. *Sci. Total Environ.* 392, 145–156.
- García-Gil, J.C., Plaza, C., Senesi, N., Brunetti, G., Polo, A., 2004. Effects of sewage sludge amendment on humic acids and microbiological properties of a semiarid Mediterranean soil. *Biol. Fertil. Soils* 39, 320–328.
- Gerardi, M.H., 2003. *The Microbiology of Anaerobic Digesters*. Wiley & Sons, Inc., Hoboken, NJ.
- Giusquiani, P.L., Pagliani, M., Gigliotti, G., Businelli, D., Benetti, A., 1995. Urban waste compost: effects on physical, chemical, and biochemical soil properties. *J. Environ. Qual.* 24, 175–182.
- Gross, A., Arusi, R., Fine, P., Nejidat, A., 2008. Assessment of extraction methods with fowl manure for the production of liquid organic fertilizers. *Bioresour. Technol.* 99, 327–334.
- Gross, A., Guy, O., Posmanik, R., Fine, P., Nejidat, A., 2012. A novel method for combined biowaste stabilization and production of nitrate-rich liquid fertilizer for use in organic horticulture. *Water Air Soil Pollut.* 223, 1205–1214.
- Hadas, A., Kautsky, L., Portnoy, R., 1996. Mineralization of composted manure and microbial dynamics in soil as affected by long-term nitrogen management. *Soil Biol. Biochem.* 28, 733–738.
- Hayes, E.T., Curran, T.P., Dodd, V.A., 2006. Odour and ammonia emissions from intensive poultry units in Ireland. *Bioresour. Technol.* 97, 933–939.
- Ho, L.C., White, P.J., 2005. A cellular hypothesis for the induction of blossom-end rot in tomato fruit. *Ann. Bot.* 95, 571–581.
- IFOAM (International Federation of Organic Agriculture), 2005. The IFOAM Norms for Organic Production and Processing (Ver. 2005). IFOAM, Germany. <http://www.ifoam.org>.
- Jun, Y., Wenfeng, X., 2009. Ammonia biofiltration and community analysis of ammonia-oxidizing bacteria in biofilters. *Bioresour. Technol.* 100, 3869–3876.
- Kelleher, B.P., Leahy, J.J., Henihan, A.M., O'Dwyer, T.F., Sutton, D., Leahy, M.J., 2002. Advances in poultry litter disposal technology – a review. *Bioresour. Technol.* 83, 27–36.
- Kelly, J.J., Policht, K., Grancharova, T., Hundal, L.S., 2011. Distinct responses in ammonia-oxidizing archaea and bacteria after addition of biosolids to an agricultural soil. *Appl. Environ. Microbiol.* 77, 6551–6558.
- Kennes, C., 1998. Waste gas biotreatment technology. *J. Chem. Technol. Biotechnol.* 72, 303–319.
- Kim, D.J., Lee, D.I., Keller, J., 2006. Effect of temperature and free ammonia on nitrification and nitrite accumulation in landfill leachate and analysis of its nitrifying bacterial community by FISH. *Bioresour. Technol.* 97, 459–468.
- Kroeze, C., 1994. Anthropogenic emissions of nitrous oxide (N_2O) from Europe. *Sci. Total Environ.* 152, 189–205.
- Kunert, W., 1922. Solubility of CO_2 and N_2O in certain Solvents. *Phys. Rev.* 19, 512–524.
- Lahav, O., Mor, T., Heber, A.J., Molchanov, S., Ramirez, J.C., Li, C., Broday, D.M., 2008. A new approach for minimizing ammonia emissions from poultry houses. *Water Air Soil Pollut.* 191, 183–197.
- Lawlor, K., Knight, B., Barbosa-Jefferson, V., Lane, P., Lilley, A., Paton, G., McGrath, S., O'Flaherty, S., Hirsch, P., 2000. Comparison of methods to investigate microbial populations in soils under different agricultural management. *FEMS Microbiol. Ecol.* 33, 129–137.
- Ling, J., Chen, S., 2005. Impact of organic carbon on nitrification performance of different biofilters. *Aquacult. Eng.* 33, 150–162.
- Mackie, R.I., Stroot, P.G., Varel, V.H., 1998. Biochemical identification and biological origin of key odor components in livestock waste. *J. Anim. Sci.* 76, 1331–1342.
- Marchaim, U., 1992. *Biogas Processes for Sustainable Development*. FAO, Rome.
- Metcalf & Eddy Inc., 2003. *Wastewater Engineering, Treatment and Reuse*, fourth ed. McGraw-Hill, New York.
- Mirzoyan, N., Parnes, S., Singer, A., Tal, Y., Sowers, K., Gross, A., 2008. Quality of brackish aquaculture sludge and its suitability for anaerobic digestion and methane production in an upflow anaerobic sludge blanket (UASB) reactor. *Aquaculture* 279, 35–41.
- Monteny, G.J., Bannink, A., Chadwick, D., 2006. Greenhouse gas abatement strategies for animal husbandry. *Agric. Ecosyst. Environ.* 112, 163–170.
- Navarro, J.M., Flores, P., Carvajal, M., Martínez, V., 2005. Changes in quality and yield of tomato fruit with ammonium, bicarbonate and calcium fertilisation under saline conditions. *J. Hort. Sci. Biotechnol.* 80, 351–357.
- Ni, J.Q., Heber, A.J., Sutton, A.L., Kelly, D.T., Patterson, J.A., Kim, S.T., 2010. Effect of swine manure dilution on ammonia, hydrogen sulfide, carbon dioxide, and sulfur dioxide releases. *Sci. Total Environ.* 408, 5917–5923.
- Nopharatana, A., Clarke, W.P., Pullammanappallil, P.C., Silvey, P., Chynoweth, D.P., 1998. Evaluation of methanogenic activities during anaerobic digestion of municipal solid waste. *Bioresour. Technol.* 64, 169–174.
- Pagans, E.L., Font, X., Sánchez, A., 2005. Biofiltration for ammonia removal from composting exhaust gases. *Chem. Eng. J.* 113, 105–110.
- Posmanik, R., Bar-Sinay, B., Golan, R., Nejidat, A., Gross, A., 2011. Reuse of stabilized fowl manure as soil amendment and its implication on organic agriculture nutrition management. *Water Air Soil Pollut.* 216, 537–545.
- Sander, R., 1999. Compilation of Henry's law constants for inorganic and organic species of potential importance in environmental chemistry (Ver. 3). <http://www.henrys-law.org>.
- Smet, E., Langenhove, H.V.A.N., Maes, K., 2000. Abatement of high concentrated ammonia loaded waste gases in compost biofilters. *Water Air Soil Pollut.* 119, 177–190.
- Soil and Plant Analysis Council, 1999. *Soil Analysis: Handbook of Reference Methods*. CRC Press LLC, Boca Raton, FL.
- Speir, T.W., Horswell, J., Schaik, A.P., McLaren, R.G., Fietje, G., 2004. Composted biosolids enhance fertility of a sandy loam soil under dairy pasture. *Biol. Fertil. Soils* 40, 349–358.
- Ulrich, G.A., Krumholz, L.R., Suflita, J.M., 1997. A rapid and simple method for estimating sulfate reduction activity and quantifying inorganic sulfides. *Appl. Environ. Microbiol.* 63, 1627–1630.
- Vymazal, J., 2007. Removal of nutrients in various types of constructed wetlands. *Sci. Total Environ.* 380, 48–65.
- Wang, Z.H., Li, S.X., Malhi, S., 2008. Effects of fertilization and other agronomic measures on nutritional quality of crops. *J. Sci. Food Agric.* 88, 7–23.

- Weiske, A., Vabitsch, A., Olesen, J., Schelde, K., Michel, J., Friedrich, R., Kaltschmitt, M., 2006. Mitigation of greenhouse gas emissions in European conventional and organic dairy farming. *Agric. Ecosyst. Environ.* 112, 221–232.
- Welander, U., Henrysson, T., Welander, T., 1998. Biological nitrogen removal from municipal landfill leachate in a pilot scale suspended carrier biofilm process. *Water Res.* 32, 1564–1570.
- Wong, J.W.C., Ma, K.K., Fang, K.M., Cheung, C., 1999. Utilization of a manure compost for organic farming in Hong Kong. *Bioresour. Technol.* 67, 43–46.
- Yapsakli, K., Aliyazicioglu, C., Mertoglu, B., 2011. Identification and quantitative evaluation of nitrogen-converting organisms in a full-scale leachate treatment plant. *J. Environ. Manage.* 92, 714–723.
- Ye, L., Peng, C.Y., Tang, B., Wang, S.Y., Zhao, K.F., Peng, Y.Z., 2009. Determination effect of influent salinity and inhibition time on partial nitrification in a sequencing batch reactor treating saline sewage. *Desalination* 246, 556–566.
- Yun, H.J., Kim, D.J., 2003. Nitrite accumulation characteristics of high strength ammonia wastewater in an autotrophic nitrifying biofilm reactor. *J. Chem. Technol. Biotechnol.* 78, 377–383.