

1 **ABSTRACT**

2

3 The performance of a biotrickling filter for the abatement of composting emissions was
4 evaluated at short gas contact times of 2 to 10 seconds with a structured and an
5 unstructured packing material. The effect of the gas contact time, pH control and water
6 make-up flowrate were also evaluated during 8 months. The average elimination capacity
7 was $13 \text{ g N m}^{-3}\text{h}^{-1}$ and $3.3 \text{ g C m}^{-3}\text{h}^{-1}$ for NH_3 and VOCs, respectively. Maximum
8 capacities obtained during an inlet concentration spiking experiment were $45 \text{ g N m}^{-3}\text{h}^{-1}$
9 and $20 \text{ g C m}^{-3}\text{h}^{-1}$, meaning a removal efficiency of 92.5 and 46.7%, respectively. A
10 decrease of 40% was detected in the nitrification capacity when the hydraulic residence
11 time increased from 2 to 5 hours. Thus, water renewal was identified as a critical
12 parameter to avoid substrate inhibition by nitrite and NH_3 accumulation. Results
13 demonstrate that significant NH_3 and VOCs removal efficiencies can be achieved for
14 composting emissions in a biotrickling filter operated at short gas contact times, which
15 entails a substantial reduction of operational and investment costs in comparison to
16 traditional techniques.

17

18 **KEY WORDS:** biotrickling filtration; composting emissions; packing materials; short
19 gas contact times; NH_3 and Volatile Organic Compounds; spiking

20

21

1 **HIGHLIGHTS:**

- 2 Operation of a BTF for composting emissions at 10 sec gas contact time.
- 3 Polyurethane foam cubes and a structured packing were compared as packing material
- 4 Average ECs of $13 \text{ g N m}^{-3}\text{h}^{-1}$ and $3.3 \text{ g C m}^{-3}\text{h}^{-1}$ were achieved for 8 months.
- 5 Water make-up flow rate affects NH_3 removal and nitrification rate.
- 6 A large packing surface area only proved useful to accelerate reactor start-up.

7

1. INTRODUCTION

Emissions from waste water treatment plants (WWTP) sludge composting facilities are characterized by high flow rates and low concentrations of several compounds, mainly ammonia (NH_3) and volatile organic compounds (VOCs). While NH_3 and amines are produced by biological degradation of urea, proteins and amino acids [1], VOCs are a large family of compounds resulting from the decomposition of organic matter at the early stages of the composting process. NH_3 emissions are the consequence of undesirable nitrogen losses from composting material and the amount emitted is determined by the $\text{NH}_3/\text{NH}_4^+$ balance, which depends on the temperature, pH and moisture content of the composting material [2]. Composting emissions of NH_3 of either the organic fraction of municipal solid wastes or anaerobically digested sludge have been reported to reach peak NH_3 concentrations between 500 and 700 $\text{mg NH}_3 \text{ m}^{-3}$, with average concentrations of around 250 $\text{mg NH}_3 \text{ m}^{-3}$, [2,3]. Instead, peak and average VOCs concentrations vary widely depending on the composted material. Peak emissions of VOCs from composting process of source-selected municipal solid wastes below 200 mg C m^{-3} have been reported while peak concentrations up to 3000 mg C m^{-3} have been found in anaerobically digested wastewater sludge composting [4]. Despite these relatively low concentrations of NH_3 and VOCs in most off-gases [4,5], they can commonly be perceived even at long distances from the source, due to their relatively low odor thresholds [6].

Several physical and chemical processes have been traditionally used to abate NH_3 and VOCs from odorous emissions, including activated carbon adsorption, wet-scrubbing, incineration and air stripping. However, high costs associated to these technologies and the possibility of secondary pollutants emissions make them uncompetitive [7]. The

1 suitability of either biofilters (BF) or biotrickling filters (BTF) have been successfully
2 tested for the abatement of NH_3 and a wide range of VOCs and conditions in lab-scale
3 studies [8–10]. However, once these techniques are applied at pilot or industrial-scale,
4 behavior can be significantly distant from that previously tested at lab-scale mainly due
5 to the variability in both the inlet flowrate and pollutants concentration commonly found
6 in industrial emissions. Indeed, the evaluation of BTF at industrial facilities for
7 composting emissions is rarely reported [11]. Smits et al. [12] applied a BTF to treat NH_3
8 and odor from a composting facility with a elimination capacity of $4 \text{ g NH}_3 \text{ m}^{-3} \text{ h}^{-1}$ and
9 an odor removal efficiency of 50%. Prado et al. [6] studied the performance of a BTF
10 during 5 months at an empty bed residence time (EBRT) of about 0.9 s as a result of an
11 industrial chemical scrubber conversion. Relatively low removal efficiencies were found
12 for VOCs and NH_3 (around 10 and 25%, respectively), corresponding to an elimination
13 capacity of $18 \text{ g C m}^{-3} \text{ h}^{-1}$ and $3 \text{ g N m}^{-3} \text{ h}^{-1}$. Mao et al. [13] concluded that BTFs were
14 better at eliminating odor, NH_3 , amines, S-compounds and VOCs than chemical scrubbers
15 and biofilters in the monitoring of three of the largest food waste composting plants of
16 Taiwan. Likewise, Xue et al. [14] found that a BTF was a promising process for the
17 treatment of complex odorous gases.

18

19 When complex mixtures of different nature are treated simultaneously, pH requirements
20 can make difficult to operate in a unique stage process. Devigny et al. [15] proposed two-
21 stage processes to first oxidize acidic compounds and to subsequently, remove VOCs in
22 a neutral pH biofilter. This could be analogous to the simultaneous treatment of NH_3 and
23 VOCs, since the water hold-up in the packed bed may significantly influence the
24 bioreactor performance. Hence, while a low water hold-up favors removal of VOCs due
25 to increased mass transport and biodegradation, a low water hold-up increases the local

1 concentration of free ammonia (FA) and free nitrous acid (FNA), which may lead to
2 inhibition of nitrification of nitrifying biomass [16]. Such limitation must be taken into
3 account in the control strategy of the process to avoid system failure. However,
4 considerable savings can be made if both kinds of compounds are removed in a single
5 reactor.

6
7 Regarding VOCs emissions, limited removal efficiencies are sometimes reported in
8 biofilters, which is related to the complexity of the VOC mixture emitted [16], the
9 hydrophobicity of most VOCs, and their variability throughout the composting process
10 [8]. Since the origin and type of waste treated in the facility determines the nature of
11 VOCs released [17], composition of process off-gases is highly specific. In the
12 performance of a food waste composting plant, Mao et al. [13] identified 29 compounds
13 and, apart from NH₃, amines and acetic acid, multiple volatile organic compounds were
14 identified (hydrocarbons, ketones, esters, terpenes and S-compounds). Similarly, Xue et
15 al. [18] detected 23 different VOCs in the exhaust gas of cattle manure composting.
16 Gallego et al. [19] monitored the indoor air from several locations of a municipal solid
17 waste treatment facility (MSWTF) in the metropolitan area of Barcelona and found an
18 equivalent range of alkanes, aromatic hydrocarbons, alcohols, aldehydes, esters and
19 terpenes. Also, Prenafeta-Boldú et al. [20] identified up to 48 different VOCs by gas
20 chromatography–mass spectrometry (GC–MS) in a full-scale composting plant in an
21 urban environment, and among them, alcohols, aldehydes, aliphatic and aromatic
22 hydrocarbons, esters, ketones, terpenes, and organosulfur compounds were detected. In
23 the case of Dorado et al. [21] more than 500 compounds were identified from the compost
24 maturation building of a MSWTF, appearing 63 of them in more than 25% of the samples.

25

1 On the other hand, another important limitation in the treatment of emissions from
2 WWTP sludge composting is the large gas flowrates to be treated, which entails large bed
3 volumes of bioreactors. Design and operation at short gas contact times is advantageous
4 in terms of costs due to reduced reactor sizing but may negatively affect VOCs abatement
5 due to mass transfer limitation caused by the low solubility of these compounds [22].

6
7 The study presented herein evaluates the performance of a BTF operated at short gas
8 contact times (2 to 10 seconds) for the abatement of composting emissions. The effect of
9 EBRT, pH control and water make-up flowrate were evaluated in a pilot-scale BTF
10 located at the WWTP of Manresa (Barcelona, Spain). The study comprises part of all
11 seasons of the year using two different synthetic support materials; one of them with a
12 structured arrangement and the other with a random structure and order. Results from this
13 study served as a starting point for setting the optimal conditions for the conversion of 3
14 chemical scrubbers to 3 biotrickling filters at an EBRT of 1.3 sec per reactor at the Cunit-
15 Cubelles WWTP (Barcelona, Spain) [23].

16

17 **2. MATERIALS AND METHODS**

18

19 The biotrickling filter (Figure 1), with a total bed height of 0.6 m and a volume of 0.5 m³
20 was monitored to determine the abatement capacity of NH₃ and VOCs using two different
21 support media. During a first period of around 4 months (from 12th April to 28th July) a
22 structured synthetic support media (FKP 158, Ecotec, Spain) with a specific surface area
23 of 420 m² m⁻³ was evaluated, corresponding from spring to summer season in the northern
24 hemisphere (average ambient temperature between 12.4 and 23.7°C). Subsequently, in
25 the period between 5th October and 12th January (from average ambient temperature of

1 14.8°C in autumn to 4.4°C in winter), the support was replaced by polyurethane foam with
2 a specific surface area of 600 m² m⁻³ (Filtren TM 25280, Recticel Iberica, Spain) and
3 monitored during the same period of time. FKP is a common packing material used for
4 chemical scrubber towers but it has also been satisfactorily tested in biotrickling filters
5 for the simultaneous removal of VOCs and H₂S from WWTP emissions [23]. A picture
6 of both packing materials can be found in the Supplementary content.

7 <Figure 1>

8

9 Both packing materials were inoculated by recirculating for 24 h sludge from the
10 nitrifying activated reactor of the same WWTP with an initial concentration of 1 g VSS
11 L⁻¹. Inlet concentrations fluctuated due to ambient temperature changes. Inlet
12 concentrations up to 90 ppmv for NH₃ and up to 130 ppmv for VOCs were detected. A
13 qualitative characterization of the composting emission was performed by CG-MS
14 detecting around 75 different compounds including acids, aldehydes, aromatics, ketones,
15 esters, ethers, furans, glycols, hydrocarbons, nitrogenous, alcohols, sulfurs, siloxanes,
16 silanes and terpenes. Gas flowrate was varied between 200 and 1200 m³ h⁻¹, which
17 corresponded to EBRTs between 2 and 10s (gas velocities between 250 and 1500 m h⁻¹).
18 The liquid phase was recirculated by means of a centrifugal pump at a velocity between
19 0.1 and 5 m h⁻¹, while the hydraulic residence time (HRT) was varied from 4 to 22.5 h.
20 The HRT is the time that water remains in the bioreactor and is calculated as the volume
21 of the water sump of the tank divided by the water make-up flowrate. A summary of the
22 main operation conditions of both materials can be found in Table 1.

23

24 <Table 1>

25

1 A structured control system with a supervisory control and data acquisition (SCADA)
2 software was used to automate the pilot plant and for data acquisition. Temperature,
3 humidity (Testo, 605-H1) and carbon dioxide (Vaisala, GMP343) were registered
4 continuously at the inlet and outlet gas stream. NH₃ and hydrogen sulfide were monitored
5 on a daily basis with an Ibrid MX6 sensor (Industrial Scientific), while a photoionization
6 detector (RAE, MiniRae 3000) was used for VOCs concentration monitoring. Pressure
7 drop across the fixed-bed reactor was measured by a water-filled U-tube manometer.
8 Temperature, pH, dissolved oxygen and oxidation-reduction potential in the liquid phase
9 were monitored online with dedicated probes (Crison), while the ionic species
10 concentrations were determined off-line by ion chromatography (Dionex, ICS1000). The
11 SCADA system was also used for controlling the aqueous phase pH to a value within 7.4
12 and 7.6 by means of either industrial water (i.e. WWTP effluent) or acid/base addition
13 (NaOH/HCl 0.1M) depending on the operating conditions tested. An auxiliary tank of 0.4
14 m³ was installed for adding additional nutrients if necessary.

15

16 At the end of each period (days 84 to 107 and 51 to 99 for FKP and PUF, respectively),
17 where low inlet VOCs concentration were detected, inlet air was artificially spiked with
18 selected VOCs with different grades of solubility (ethanol, hexane and toluene) to
19 evaluate the performance of the BTF under more steady conditions. Each compound was
20 individually tested by continuous addition of a pure liquid VOC to reach an inlet
21 concentration of 20 ppmv in the air stream. To evaluate the performance of the BTF in
22 terms of N removal, the nitrification percentages were calculated as the ratio of the mass of
23 nitrite and nitrate with respect to the sum of all nitrogen species. In addition, the
24 nitrification percentages were determined as the fraction of nitrate with respect to the sum

1 of nitrate and nitrite. Nitritation (R_1) and nitrataion (R_2) rates were calculated based on
2 Baquerizo et al [9].

3

4 **3. RESULTS AND DISCUSSION**

5

6 **3.1. Operation with the structured support material**

7

8 The BTF performance was evaluated with the structured packing material (FKP) during
9 almost 4 months of operation working without interruptions (Figure 2). Results obtained
10 during monitoring of the plant were subjected to high concentration fluctuations observed
11 along the whole operation and related with normal fluctuations in industrial sites (from
12 13 to 89 ppm_v for NH₃ and between 0 and 133 ppm_v for VOCs).

13

14 <Figure 2>

15

16 The average removal efficiency (RE) for nitrogen was 82%, corresponding to an
17 elimination capacity (EC) of 13 g N m⁻³h⁻¹, while for VOCs the average RE and EC were
18 46% and 3.3 g C m⁻³h⁻¹, respectively. The complexity of the VOCs emitted [24], the large
19 inlet concentration fluctuations (between 0 and 133 ppm_v) (Figure 2) and the lack of
20 sorption capacity to buffer such fluctuations probably limited the REs achieved.
21 Considering data of the doping process, from day 85, the system showed an average EC
22 of 5,2 g C m⁻³h⁻¹ and a punctual maximum EC of 20 g C m⁻³h⁻¹ (RE of 46,7%) when
23 concentrations were increased under more steady conditions (between 4 and 35 ppm) .
24 The critical and the maximum EC for NH₃ was not achieved at the operation conditions
25 of the plant, since at the maximum NH₃ inlet load monitored at the plant, the efficiency

1 was 100%; thus it can be affirmed the maximum EC was over $45 \text{ g N m}^{-3}\text{h}^{-1}$. The EC
2 versus the inlet load is plotted latter in the comparison of packing materials in section 3.2
3 (Figure 6A). A critical EC of $45 \text{ g N m}^{-3}\text{h}^{-1}$ and a maximum EC between $50\text{-}100 \text{ g N m}^{-3}\text{h}^{-1}$
4 h^{-1} have been previously reported for BTF in NH_3 abatement [25], although contact times
5 used (13.5s) were higher than those tested in the present study (between 2 and 10s).
6
7 REs increased during the first weeks to reach a maximum RE of 95% for NH_3 20 days
8 after the startup, which showed a more stable inlet load than VOCs (Figure 2). ECs for
9 NH_3 were increasing progressively during the first month of operation up to $45 \text{ g N m}^{-3}\text{h}^{-1}$
10 1 , which was also related with an increase of the inlet concentration (from 15 to 90 ppm)
11 according to air temperatures during the seasonal changes. When the impact of odorous
12 emissions, derived from the low bioreactor performance during startup phases, is not
13 permitted, the use of a selective inoculum can reduce this phase. Hernández et al. [10]
14 reported a shorter startup of 14 days for the biofiltration of NH_3 and a mixture of VOCs
15 by inoculating the packing material with an enriched microbial population at an EBRT of
16 25s. Xue et al. [26] obtained an increase in RE of 15% when the BTF was inoculated with
17 nitrifying bacteria in a BTF treating NH_3 emitted from the exhaust gases of cattle manure
18 compost.
19
20 Reducing the contact time is an interesting option to reduce the bed volume and,
21 consequently, investment costs. However, mass transfer limitation can reduce the
22 suitability of BTFs for specific scenarios, for instance in the removal of high H_2S loads
23 due to an oxygen transfer limitation and consequently, partial oxidation [27]. Results
24 presented herein show that high efficiencies can be achieved for NH_3 with contact times
25 between 2 and 10 s. However, the effect of EBRT became critical below 2 seconds where

1 the mass transfer became limiting and the elimination decreased drastically. Figure 3a
2 shows the effect of contact time on RE for NH₃. Inconclusive results were found for
3 VOCs since a clear relationship with the EBRT was not observed (data not shown) mainly
4 due to the high variability of the inlet load and periods of starvation, e.g. from day 48 to
5 56 (Figure 2). RE for VOCs were in general moderate but a slightly improvement was
6 observed during the start-up when concentrations progressively increased. Thus, under
7 more stable inlet conditions and time to biomass acclimation, larger REs could be
8 achieved, as it has been previously reported in the biofiltration of toluene [28]. During
9 the latest 20 days of operation at higher inlet concentrations, after a long period of
10 starvation and without new inoculation, an average RE of 60% was achieved.

11 <Figure 3>

12
13 Concentrations of nitrite and nitrate in the aqueous phase up to 1600 and 400 mg N L⁻¹,
14 respectively, indicated that NH₃ was not only being absorbed but it was also biologically
15 oxidized (Figure 3B). Mass balances showed that the average nitrification and nitrification
16 percentages were 73% and 46%, respectively. Dissolved oxygen concentration was never
17 below 3.5 mg DO L⁻¹, indicating that oxygen-limiting conditions did not occur during the
18 operation. A high accumulation of ammonium and nitrite occurred between day 30 and
19 34 corresponding to a low aqueous phase renovation due to low water requirements for
20 pH control. At this stage, pH was self-regulated because of the balance of proton
21 consumption between basification due to ammonia absorption and acidification due to
22 nitrification. From day 34 on, when ammonium and nitrite accumulated, the NH₃ EC
23 decreased progressively from 30 g N m⁻³ h⁻¹ to a steady removal of 15 g N m⁻³ h⁻¹. From
24 day 48 on, water flowrate was kept constant at around 90 L h⁻¹ and the pH was controlled
25 by means of chemical reagents obtaining subsequently a slight recovery of RE. The drop

1 in NH_3 RE observed in Figure 2 between day 56 and 60 also correlated with higher
2 concentration of ammonium and nitrite in the liquid phase (above 500 ppm N for both
3 species).

4
5 Baquerizo et al. [9] monitored NH_3 removal in a biofilter packed with coconut fiber
6 observing low nitrataion and nitrification rates in relation with large amounts of FA and
7 FNA accumulated in the packed bed, thus causing inhibition episodes on ammonium-
8 oxidizing bacteria (AOB) and/or nitrite-oxidizing bacteria (NOB). Similarly, Hernández
9 et al. [10] detected inhibition of certain VOCs such as methylmercaptan by FA and FNA
10 in the biofiltration of a gas mixture containing NH_3 and different VOCs. At the present
11 operation conditions of temperature and pH the free ammonia (FA) concentration
12 calculated in the liquid was $1.98 \text{ mg FA L}^{-1}$. It has been stated that this form causes
13 microbial inhibition, rather than ammonium [29]. Jubany et al. [30] reported inhibition
14 thresholds of 7.0 and $0.95 \text{ mg FA L}^{-1}$ for AOB and NOB, respectively. Results clearly
15 show that inhibition occurred under these conditions, especially for the nitrataion step,
16 which should be avoided to guarantee an optimal operation.

17
18 Figure 4 shows the effect of the hydraulic residence time (HRT) on EC for NH_3 , the
19 nitrification rate (R_1) and the ratio nitrataion/nitrification rate (R_2/R_1). The R_2/R_1 ratio
20 corresponds to the ratio between the amounts of nitrate and nitrite produced in the reactor
21 per unit of reactor volume and time. Hence, a R_2/R_1 ratio close to 1 indicates full
22 nitrification (to nitrate), while a R_2/R_1 ratio close to 0 represents predominance of partial
23 nitrification (to nitrite). Results show that at short HRT the NH_3 EC varied in a wide range
24 from 2 to $45 \text{ g m}^{-3}\text{h}^{-1}$. Despite of the large variability in the EC of NH_3 , absorption may
25 be negatively affected at low renovation rate because of the inhibition of the biological

1 process due to FA accumulation. Thus, a reduced gradient is found between the gas and
2 the liquid phase for NH_3 absorption. A decrease of 40 % was detected in the ratio R_2/R_1
3 when the HRT increased from 2 to 5 hours. The minimum ratio R_2/R_1 was 0.22 at HTR
4 above 20 hours. Thus, the nitrataion rate decreased exponentially as the water phase
5 renewal decreased, indicating that nitrataion was more affected than nitrification at high
6 HRT due to an increase in inhibitory concentrations and a higher sensitivity of the second
7 step of the nitrification [29].

8

9 <Figure 4>

10

11 Most studies focusing on NH_3 biofiltration show that pH control together with the
12 maintenance of an optimal water content in the filter bed arise as key operating parameters
13 in order to keep a stable operation [7]. On the other hand, VOCs are degraded by
14 heterotrophic microorganisms, which are thought to be most effective at neutral pH [31].
15 Due to their configuration and controllability, biotrickling filters appear as a better
16 alternative than biofilters when NH_3 is the main pollutant to be treated [25]. In the case
17 of biotrickling filters, the water content is ensured with the continuous recirculation of a
18 liquid phase, so pH control is the key parameter to guarantee the optimal operation.
19 Among different control strategies to keep an optimal pH, present study entails how the
20 use of industrial water can arise negative consequences in the biological system in relation
21 to episodes of low water renovation and the consequently accumulation of inhibitory
22 species. Taking this into consideration, the operation with PUF material was performed
23 keeping a minimum HRT of 5 hours through a fixed make-up water supply and
24 controlling the pH by means of reagents.

25

3.2. Operation with the unstructured support material

The use of polyurethane foam has been satisfactorily reported for short contact times of this magnitude for the removal of hydrogen sulfide and odorous compounds in BTF [32]. Figure 5 shows the evolution of the nitrogen RE for PUF (Figure 5A). Concentrations of nitrogenous species in the liquid phase during this period are shown in Figure 5B jointly with the corresponding extent of the biological oxidation rates (R_1/R_2).

<Figure 5>

In comparison with results obtained with the FKP material (Figure 2), the start-up with PUF was considerably faster. The time needed to achieve steady conditions at complete RE was reduced from 28 to 16 days. It is noteworthy that the main differences between materials lay in their specific surface area (420 and $600 \text{ m}^2 \text{ m}^{-3}$ for FKP and PUF, respectively) as well as in the distribution of the void space due to the structured or unstructured arrangement. Both factors affect biomass and water retention. However, pressure drop monitored during operation did not denote remarkable differences (from 4 to $16 \text{ mmH}_2\text{O m}^{-1}$).

Focusing on nitrogenous species detected in the liquid phase (Figure 5B), it is noteworthy that all NH_3 transferred from the gas was not only absorbed but also biodegraded obtaining complete oxidation to nitrate from day 12 onward. Unlike operation with the structured support, nitrite accumulation was not detected in the whole period avoiding any possibility to inhibit the process. Nitrogen mass balances calculated from NH_3 , NH_4^+ , NO_2^- and NO_3^- measurements, indicated that after the initial start-up and before day 50 the

1 outlet nitrogen content was above the nitrogen fed. Thus, after a previous phase of
2 ammonia absorption, the nitrogen accumulated was nitrified. However, this trend
3 changed latter, when the nitrogen mass balance indicated the opposite behavior since part
4 of the nitrogen supplied was not detected neither in the outlet nor in any of the oxidized
5 species. Nitrogen mass balance deviations are often observed for ammonia removal by
6 biofiltration [33]. Some studies have indicated that denitrification, in which nitrite and
7 nitrate are reduced into nitrogen gas, could also take place (autotrophically or
8 heterotrophically) [34]. Nitrifiers are known to produce NO and N₂O under the stress of
9 oxygen-limited conditions. Chen et al. [33] concluded that nitrifiers produce NO and N₂O
10 in response to other stresses such as low pH and high NH₃ and nitrite concentrations,
11 which was a more feasible explanation in our study taking into account the relatively high
12 dissolved oxygen concentration (> 3 mg DO L⁻¹) found in the liquid phase of the
13 biotrickling filter .

14

15 To compare the different behavior in the performance of both packing materials
16 (structured and unstructured) nitrogen elimination capacity versus NH₃ inlet load was
17 plotted in Figure 6A. Similarly, the most noteworthy differences in the removal of volatile
18 organic compounds can be observed between Figure 6B for PUF and Figure 2 for FKP.
19 EC for VOCs versus inlet load can be also found in the Supplementary Information for
20 both materials. Although both materials were operated under the same conditions of
21 EBRT and HRT, inlet loads, which depended mainly on ambient air, were significantly
22 different due to the different season where they were performed. During operation with
23 FKP, the average inlet concentration was 40 ppm for NH₃ and very variable (from 5 to
24 140 ppm) for VOCs, corresponding to inlet loads up to 50 gN m⁻³h⁻¹ and 250 gC m⁻³h⁻¹.
25 Emissions from maturation piles depend on the pile temperature which is affected by the
26 air temperature and the air renovation rate. During the operation with PUF, the ambient

1 temperature decrease from 23.7 up to 4.4°C and the inlet load varied between 0 and 5.5
2 $\text{gN m}^{-3}\text{h}^{-1}$ in the case of NH_3 and from 0 to 15 $\text{gC m}^{-3}\text{h}^{-1}$ in the case of VOCs. Moreover,
3 temperature in biofilters, as well as biological activity, is largely influenced by the
4 temperature of the gas treated since air is forced to pass through the packed bed of the
5 biofilter. In consequence, the lower temperature of the off-gases treated along winter
6 period which, concomitantly, meant a reduced biological activity in the biofiltration
7 system lead to reduced RE along cold periods for PUF [21]. Moreover, it has been
8 reported that at higher NH_3 loads, VOCs removal is enhanced [35], which could suppose
9 a case of nutrient limitation in the present study at these low NH_3 concentrations. Morales
10 et al. [35] observed an increase from 8 to 30 $\text{g m}^{-3}\text{h}^{-1}$ in the EC for toluene after the
11 addition of gaseous ammonia as evidence of nutrient limitation. Otherwise, when NH_3
12 concentration exceeds the boundary of 150 ppm_v , VOCs removal can be inhibited [36].

13

14

<Figure 6>

15

16 Comparing the start-ups in the removal of NH_3 and VOCs in the PUF reactor, a shorter
17 startup time was found for NH_3 removal compared to that for VOCs, which is in
18 agreement with previously reported works [37]. Due to the high fluctuations observed for
19 VOCs, inlet load was spiked from day 51 with different organic compounds with different
20 solubility (ethanol, hexane and toluene). Figure 6B shows that when a soluble compound
21 as ethanol was supplied, the elimination capacity increased quickly from 0.5 to more than
22 $4 \text{ g m}^{-3} \text{ h}^{-1}$ (100% of the inlet load). In this case, even at these short contact times (around
23 6 sec), this material becomes efficient to transfer the pollutant from the gas phase. When
24 other less soluble pollutants were supplied, i.e. the case of hexane from day 65, the
25 removal decreased drastically. However, when toluene was subsequently fed, the
26 elimination improved immediately again up to $4 \text{ g m}^{-3} \text{ h}^{-1}$, although a long starvation

1 period of 10 days took place previously. Although mass transfer limitation would be still
2 the main limiting factor for their abatement, it is expected that with longer periods of
3 acclimation, efficiencies could be significantly enhanced,. It also should be considered
4 that ethanol can inhibit the activity of microorganisms and, thus, affect the posterior
5 performance for the subsequently compounds evaluated. These results do not differ
6 significantly from those obtained with the structured support (Figure 2). Mainly, with
7 FKP material, the RE obtained during the pollutant spiking period were relatively larger,
8 which could be related with the previous acclimation of biomass at higher VOC
9 concentrations during the operation. Apart from that, this observation indicates that main
10 differences only become evident during the start-up of the process, but once the biomass
11 is immobilized onto the material and adapted at the new conditions, variances between
12 them were imperceptible.

13

14

15 **4. CONCLUSIONS**

16

17 This study constitutes, to the best of our knowledge, the first evaluation of a biotrickling
18 filter at pilot plant scale for the simultaneous abatement of NH_3 and volatile organic
19 compounds at contact times shorter than 10 seconds. This study underlines how in the
20 biofiltration of WWTP sludge composting emissions water renovation becomes a critical
21 parameter to avoid inhibition by FA and FNA accumulation. Control of pH by means of
22 sole industrial water addition can become counterproductive when low water flow is
23 needed to keep the optimal pH of operation. To avoid this strong dependence, it has been
24 found that it is desirable to keep a water renovation rate and to control the pH by means
25 of acid/basic solutions addition. Present results highlight how the aqueous phase

1 renovation directly affects the grade of NH₃ removal and the nitrification achieved in the
2 system. On the contrary, VOCs removal did not show a clear relation with this operational
3 parameter which is consistent with their higher hydrophobic character.

4
5 In the comparison of the two different synthetic packing materials, this study emphasizes
6 that the higher specific surface area of the PUF only accelerates the start-up of the process
7 obtaining similar results during the rest of the operation. Thus, once the support is
8 colonized by the biomass the advantaged of the material with higher specific surface area
9 becomes meaningless under the operating conditions tested.

10
11 Results presented herein demonstrate that significant REs can be achieved by a
12 biotrickling filter at short contact times for treating low-load composting emissions.
13 Although further research is needed to assess the individual performance of different
14 VOCs, biotrickling filters to treat low-loads of NH₃ and VOCs can be seen as an
15 alternative to be evaluated versus the traditional combination of chemical scrubbing and
16 conventional biofiltration where NH₃ is abated in the former, and VOCs are degraded
17 subsequently. The use of a single biotrickling filter with relative low volume entails a
18 substantial reduction of operational and investment costs for composting emissions
19 treatment.

20 21 **ACKNOWLEDGEMENTS**

22
23 This study was funded by the company ECOTEC-Ecología Técnica S.A. (Spain). Authors
24 also acknowledge the invaluable collaboration of PhD students Xavier Guimerà, Javier
25 Muñoz and Ginesta Rodríguez for the monitoring of the plant.

1

2 REFERENCES

- 3 [1] Hort C, Gracy S, Platel V, Moynault L. Evaluation of sewage sludge and yard
4 waste compost as a biofilter media for the removal of ammonia and volatile
5 organic sulfur compounds (VOSCs). *Chem Eng J* 2009;152:44–53.
6 doi:10.1016/j.cej.2009.03.026.
- 7 [2] Pagans E, Barrena R, Font X, Sánchez A. Ammonia emissions from the
8 composting of different organic wastes. Dependency on process temperature.
9 *Chemosphere* 2006;62:1534–42. doi:10.1016/j.chemosphere.2005.06.044.
- 10 [3] Haug RT. *The Practical Handbook of Compost Engineering*. Boca Raton, Fla.:
11 Lewis Publishers; 1993.
- 12 [4] Colon J, Martinez-Blanco J, Gabarrell X, Rieradevall J, Font X, Artola A, et al.
13 Performance of an industrial biofilter from a composting plant in the removal of
14 ammonia and VOCs after material replacement. *J Chem Technol Biotechnol*
15 2009;84:1111–7. doi:10.1002/jctb.2139.
- 16 [5] Papurello D, Soukoulis C, Schuhfried E, Cappellin L, Gasperi F, Silvestri S, et al.
17 Monitoring of volatile compound emissions during dry anaerobic digestion of the
18 Organic Fraction of Municipal Solid Waste by Proton Transfer Reaction Time-
19 of-Flight Mass Spectrometry. *Bioresour Technol* 2012;126:254–65.
20 doi:10.1016/j.biortech.2012.09.033.
- 21 [6] Prado ÓJ, Redondo RM, Lafuente J, Gabriel D. Retrofitting of an Industrial
22 Chemical Scrubber into a Biotrickling Filter: Performance at a Gas Contact Time
23 below. *J Environ Eng* 2009;135:359–66. doi:10.1061/(ASCE)EE.1943-
24 7870.0000013.
- 25 [7] Chung YC, Huang C, Tseng CP. Biotreatment of ammonia from air by an
26 immobilized *Arthrobacter oxydans* CH8 biofilter. *Biotechnol Prog* 1997;13:794–
27 8. doi:10.1021/bp970065e.
- 28 [8] Pagans E, Font X, Sánchez A. Coupling composting and biofiltration for
29 ammonia and volatile organic compound removal. *Biosyst Eng* 2007;97:491–
30 500. doi:10.1016/j.biosystemseng.2007.03.035.
- 31 [9] Baquerizo G, Maestre JP, Machado VC, Gamisans X, Gabriel D. Long-term
32 ammonia removal in a coconut fiber-packed biofilter: Analysis of N fractionation
33 and reactor performance under steady-state and transient conditions. *Water Res*
34 2009;43:2293–301. doi:10.1016/j.watres.2009.02.031.
- 35 [10] Hernandez J, Prado OJ, Almarcha M, Lafuente J, Gabriel D, Hernández J, et al.
36 Development and application of a hybrid inert/organic packing material for the
37 biofiltration of composting off-gases mimics. *J Hazard Mater* 2010;178:665–72.
38 doi:10.1016/j.jhazmat.2010.01.137.

- 1 [11] Xue N, Wang Q, Wu C, Sun X, Xie W. A pilot field-scale study on biotrickling
2 filter treatment of NH₃-containing odorous gases from organic waste composting
3 plants. *J Zhejiang Univ Sci A* 2010;11:629–37. doi:10.1631/jzus.A1000095.
- 4 [12] Smits MCJ, Hoek AP, Osinga B, Ottengraf SPP, Wijngaard M. Removal of
5 ammonia and odour from composting facility waste gas with a bio-trickling filter.
6 *Proc. Ninth Forum Appl. Biotechnol., Gent, Belgium: 1995*, p. 2313–20.
- 7 [13] Mao I-F, Tsai C-J, Shen S-H, Lin T-F, Chen W-K, Chen M-L. Critical
8 components of odors in evaluating the performance of food waste composting
9 plants. *Sci Total Environ* 2006;370:323–9. doi:10.1016/j.scitotenv.2006.06.016.
- 10 [14] Xue N, Wang Q, Wang J, Wang J, Sun X. Odorous composting gas abatement
11 and microbial community diversity in a biotrickling filter. *Int Biodeterior*
12 *Biodegradation* 2013;82:73–80. doi:10.1016/j.ibiod.2013.03.003.
- 13 [15] Deviny JS, Chitwood DE, Reynolds FE. Proceedings of the 91st Annual
14 Meeting and Exhibition on Air and Waste Management Association. *Proc. 91st*
15 *Annu. Meet. Exhib. Air Waste Manag. Assoc., San Diego: 1998*, p. 11.
- 16 [16] Papurello D, Lanzini A, Leone P, Santarelli M, Silvestri S. Biogas from the
17 organic fraction of municipal solid waste: Dealing with contaminants for a solid
18 oxide fuel cell energy generator. *Waste Manag* 2014;34:2047–56.
19 doi:10.1016/j.wasman.2014.06.017.
- 20 [17] Chiriac R, Carre J, Perrodin Y, Fine L, Letoffe J-M. Characterisation of VOCs
21 emitted by open cells receiving municipal solid waste. *J Hazard Mater*
22 2007;149:249–63. doi:10.1016/j.jhazmat.2007.07.094.
- 23 [18] Xue N, Wang Q, Wu C, Zhao P, Xie W. Elimination of NH₃ and odor from
24 composting by biotrickling filter and preliminary exploration on molecular
25 biology. *Water Sci Technol* 2011;63:747–53. doi:10.2166/wst.2011.302.
- 26 [19] Gallego E, Roca FJ, Perales JF, Sánchez G, Esplugas P. Characterization and
27 determination of the odorous charge in the indoor air of a waste treatment facility
28 through the evaluation of volatile organic compounds (VOCs) using TD-GC/MS.
29 *Waste Manag* 2012;32:2469–81. doi:10.1016/j.wasman.2012.07.010.
- 30 [20] Prenafeta-Boldú F, Ortega O, Arimany M, Canalias F. Assessment of process
31 limiting factors during the biofiltration of odorous VOCs in a full-scale
32 composting plant. *Compost Sci Util* 2012;20:73–8.
- 33 [21] Dorado AD, Husni S, Pascual G, Puigdemívol C, Gabriel D. Inventory and
34 treatment of compost maturation emissions in a municipal solid waste treatment
35 facility. *Waste Manag* 2014;34:344–51. doi:10.1016/j.wasman.2013.10.044.
- 36 [22] Dorado AD, Rodríguez G, Ribera G, Bonsfills A, Gabriel D, Lafuente J, et al.
37 Evaluation of Mass Transfer Coefficients in Biotrickling Filters: Experimental
38 Determination and Comparison to Correlations. *Chem Eng Technol*
39 2009;32:1941–50. doi:10.1002/ceat.200900275.

- 1 [23] Santos A, Guimerà X, Dorado AD, Gamisans X, Gabriel D, Xavier GG, et al.
2 Conversion of chemical scrubbers to biotrickling filters for VOCs and H₂S
3 treatment at low contact times. *Biotech Air Pollut Control Bioenergy*
4 2014;99:193–203. doi:10.1007/s00253-014-5796-2.
- 5 [24] Pagans E, Font X, Sánchez A. Emission of volatile organic compounds from
6 composting of different solid wastes: abatement by biofiltration. *J Hazard Mater*
7 2006;131:179–86. doi:10.1016/j.jhazmat.2005.09.017.
- 8 [25] Sakuma T, Jinsiriwanit S, Hattori T, Deshusses M a. Removal of ammonia from
9 contaminated air in a biotrickling filter - denitrifying bioreactor combination
10 system. *Water Res* 2008;42:4507–13. doi:10.1016/j.watres.2008.07.036.
- 11 [26] Xue N, Wang Q, Wu C, Zhang L, Xie W. Enhanced removal of NH₃ during
12 composting by a biotrickling filter inoculated with nitrifying bacteria. *Biochem*
13 *Eng J* 2010;51:86–93. doi:10.1016/j.bej.2010.05.007.
- 14 [27] Rodriguez G, Dorado ADA, Fortuny M, Gabriel D, Gamisans X. Biotrickling
15 filters for biogas sweetening: Oxygen transfer improvement for a reliable
16 operation. *Process Saf Environ Prot* 2014;92:261–8.
17 doi:10.1016/j.psep.2013.02.002.
- 18 [28] Dorado AD, Baeza JA, Lafuente J, Gabriel D, Gamisans X. Biomass
19 accumulation in a biofilter treating toluene at high loads – Part 1: Experimental
20 performance from inoculation to clogging. *Chem Eng J* 2012;209:661–9.
21 doi:10.1016/j.cej.2012.08.018.
- 22 [29] Anthonisen AC, Loehr RC, Prakasam TBS, Srinath EG. Inhibition of nitrification
23 by ammonia and nitrous acid. *J Water Pollut Fed* 1976;48:835–52.
- 24 [30] Jubany I, Carrera J, Lafuente J, Baeza JA. Start-up of a nitrification system with
25 automatic control to treat highly concentrated ammonium wastewater:
26 experimental results and modelling. *Chem Eng J* 2008;144:407–19.
- 27 [31] Cox H. Co-treatment of H₂S and toluene in a biotrickling filter. *Chem Eng J*
28 2002;87:101–10. doi:10.1016/S1385-8947(01)00222-4.
- 29 [32] Gabriel D, Araya D, Brown J, Torres E, Deshusses MA. Short contact time
30 biotrickling filters for odor treatment: performance of a full-scale reactor at
31 Orange County Sanitation District. *Proc., 2002 USC-TRG Conf. Biofiltration Air*
32 *Pol. Control*, Los Angeles: University of Southern California; 2002, p. 267–76.
- 33 [33] Chen Y-X, Yin J, Wang K-X. Long-term operation of biofilters for biological
34 removal of ammonia. *Chemosphere* 2005;58:1023–30.
35 doi:10.1016/j.chemosphere.2004.09.052.
- 36 [34] Joshi J a, Hogan J a, Cowan RM, Strom PF, Finstein MS. Biological removal of
37 gaseous ammonia in biofilters: space travel and earth-based applications. *J Air*
38 *Waste Manag Assoc* 2000;50:1647–54. doi:10.1080/10473289.2000.10464189.

- 1 [35] Morales M, Revah S, Auria R. Start-up and the effect of gaseous ammonia
2 additions on a biofilter for the elimination of toluene vapors. *Biotechnol Bioeng*
3 1998;60:483–91.
- 4 [36] Smet E, Van Langenhove H. Abatement of volatile organic sulfur compounds in
5 odorous emissions from the bio-industry. *Biodegradation* 1998;9:273–84.
- 6 [37] Galera MM, Cho E, Tuuguu E, Park S-J, Lee C, Chung W-J. Effects of pollutant
7 concentration ratio on the simultaneous removal of NH₃, H₂S and toluene gases
8 using rock wool-compost biofilter. *J Hazard Mater* 2008;152:624–31.
9 doi:10.1016/j.jhazmat.2007.07.025.

10

11

1 **FIGURE LEGENDS**

2

3 *Figure 1. Diagram of the pilot plant. A and B are the sampling ports for gas phase at the*
4 *inlet and outlet stream and equivalently, C and D for the liquid phase. Discontinuous*
5 *lines represent electrical signal. Instrumentation is indicated with the following*
6 *nomenclature: temperature (TI), flowrate (FI), humidity (HI), Redox (RdI), dissolved*
7 *oxygen (ODI), carbon dioxide (AI), level (LI) and alarm level indicators (LAL). pH*
8 *indicator (pHI), pH transmitter (pHT) and pH controller (pHC).*

9

10 *Figure 2. Removal efficiency (RE), elimination capacity (EC) and inlet concentration*
11 *(C_{in}) along time for structured support where X is nitrogen or carbon. RE is the*
12 *percentage of mass removed in the biofilters. EC is the total mass abated per unit of*
13 *reactor volume and time.*

14

15 *Figure 3. Effect of the empty bed residence time on NH₃ removal efficiency (A) and*
16 *ammonium, nitrite and nitrate concentrations in the liquid along operation time (B).*

17

18 *Figure 4: Effect of hydraulic residence time (HRT) on nitrification rate (R₁), nitrification-*
19 *nitrification rate (R₂/R₁) and elimination capacity (EC) for NH₃ and VOCs.*

20

21 *Figure 5: Evolution of NH₃ load and the corresponding elimination capacity in the*
22 *performance of PUF as packing material (A) and nitrogenous species monitored in the*
23 *liquid (B).*

24

25 *Figure 6: NH₃ EC versus the load for the two packing materials (A) and the evolution of*
26 *VOCs elimination capacity and removal efficiency in the BTF packed with PUF (B).*

1

2

3

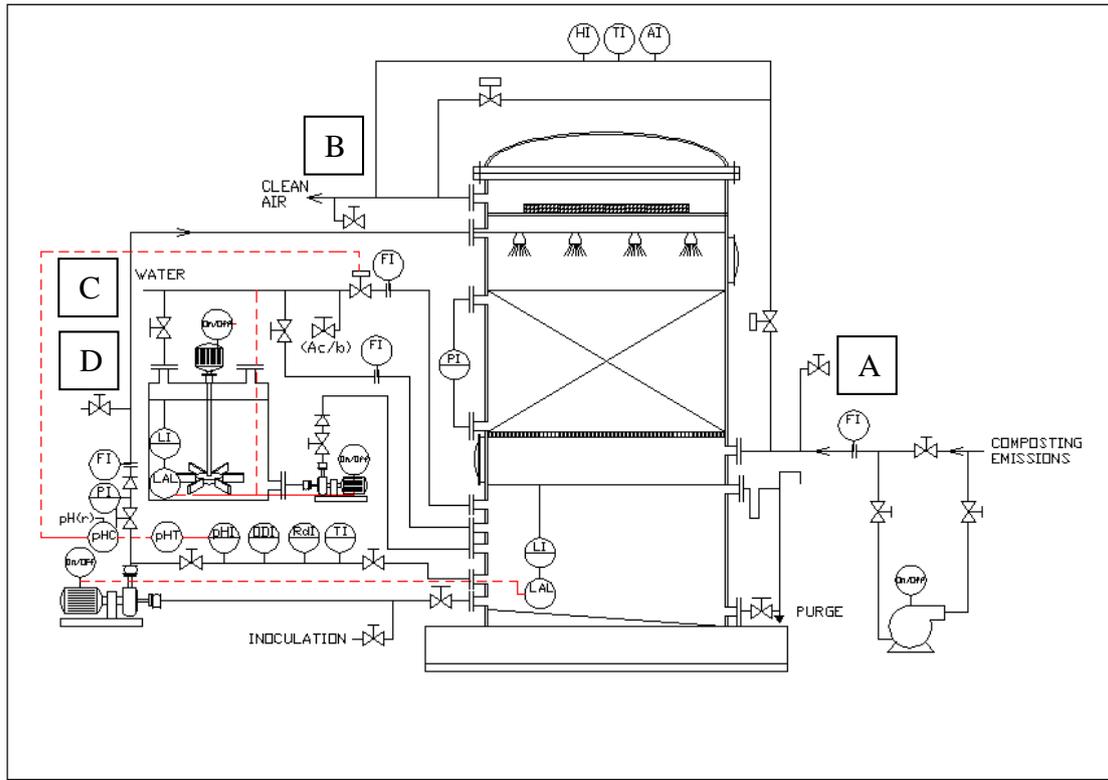
4

5

6

1
2

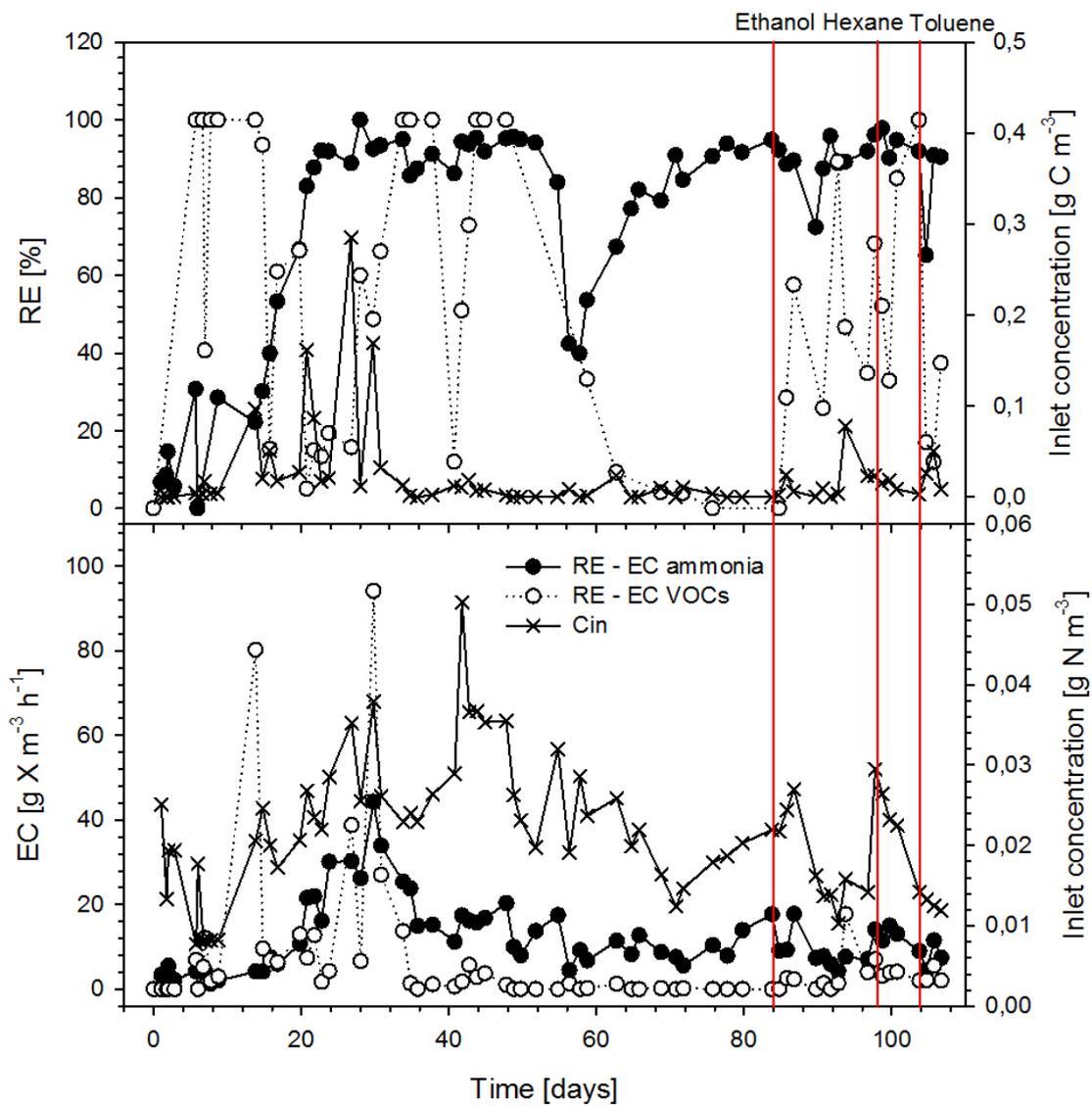
Figure 1



3
4

1

Figure 2



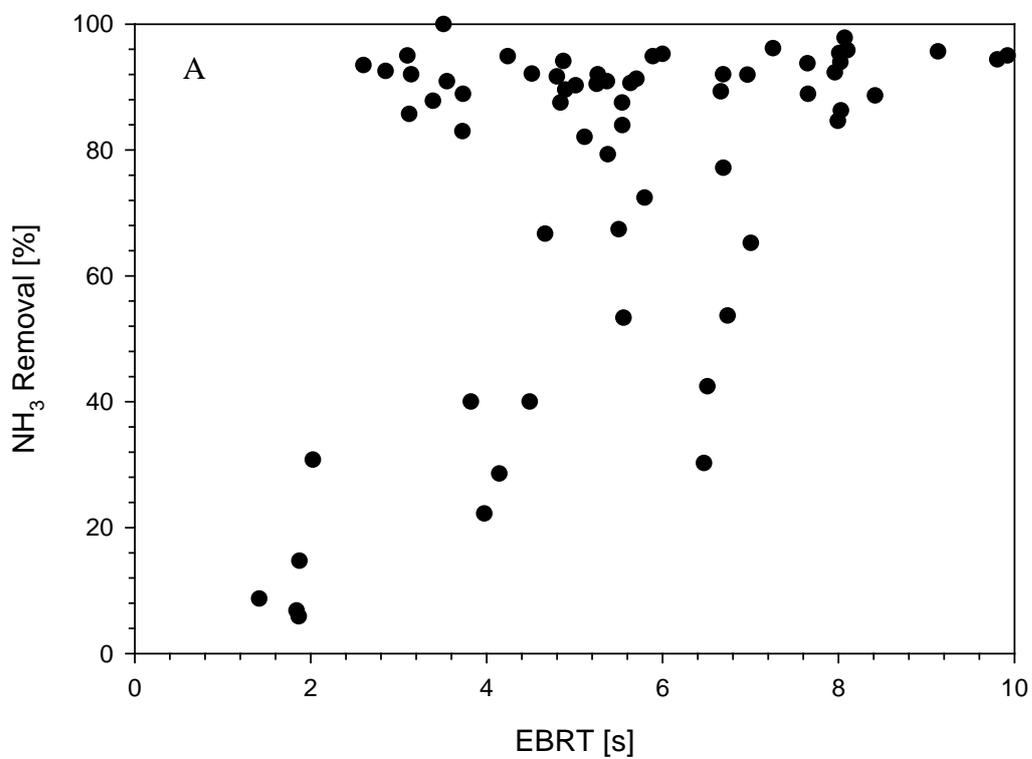
2

3

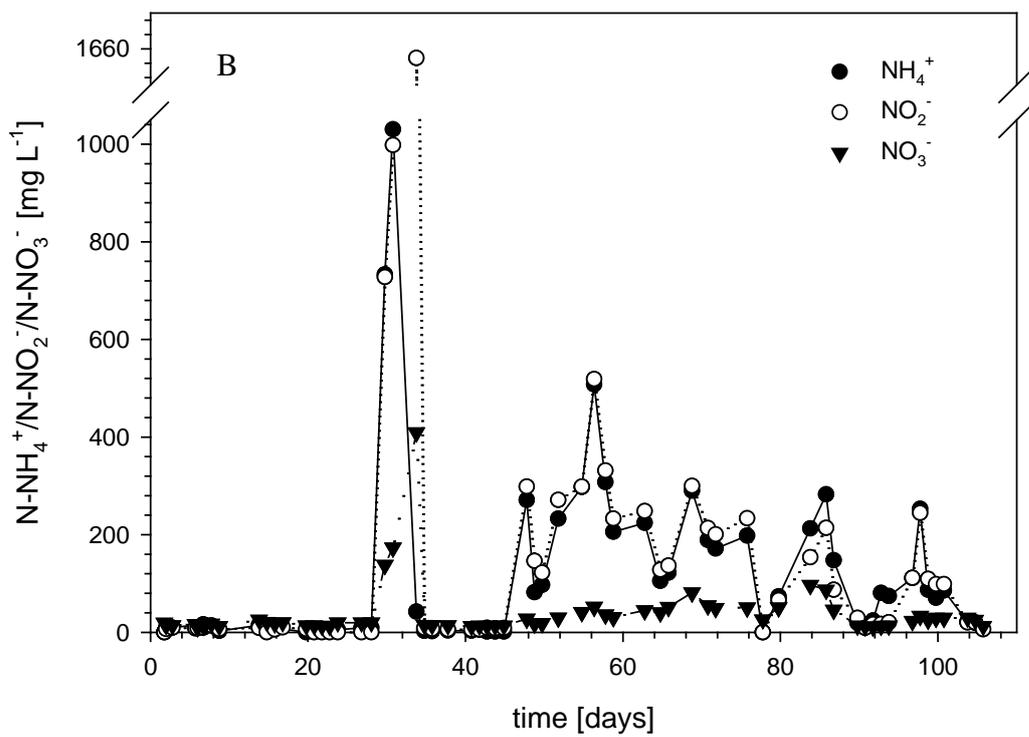
4

1

Figure 3



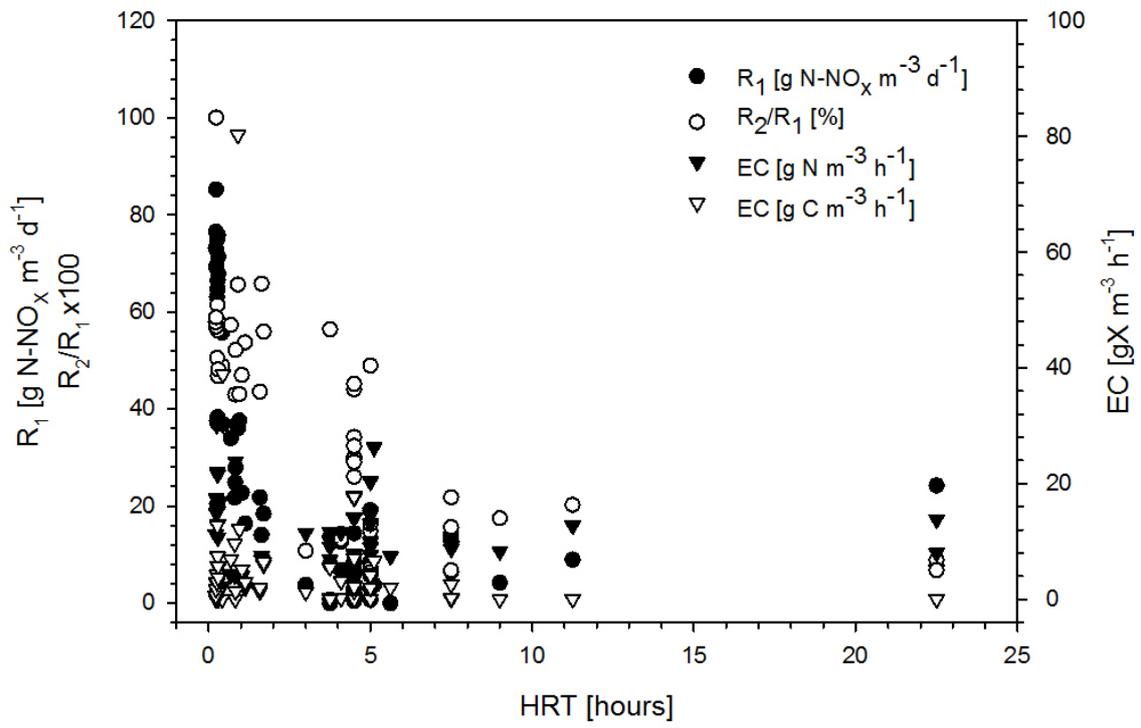
2



3

1
2

Figure 4

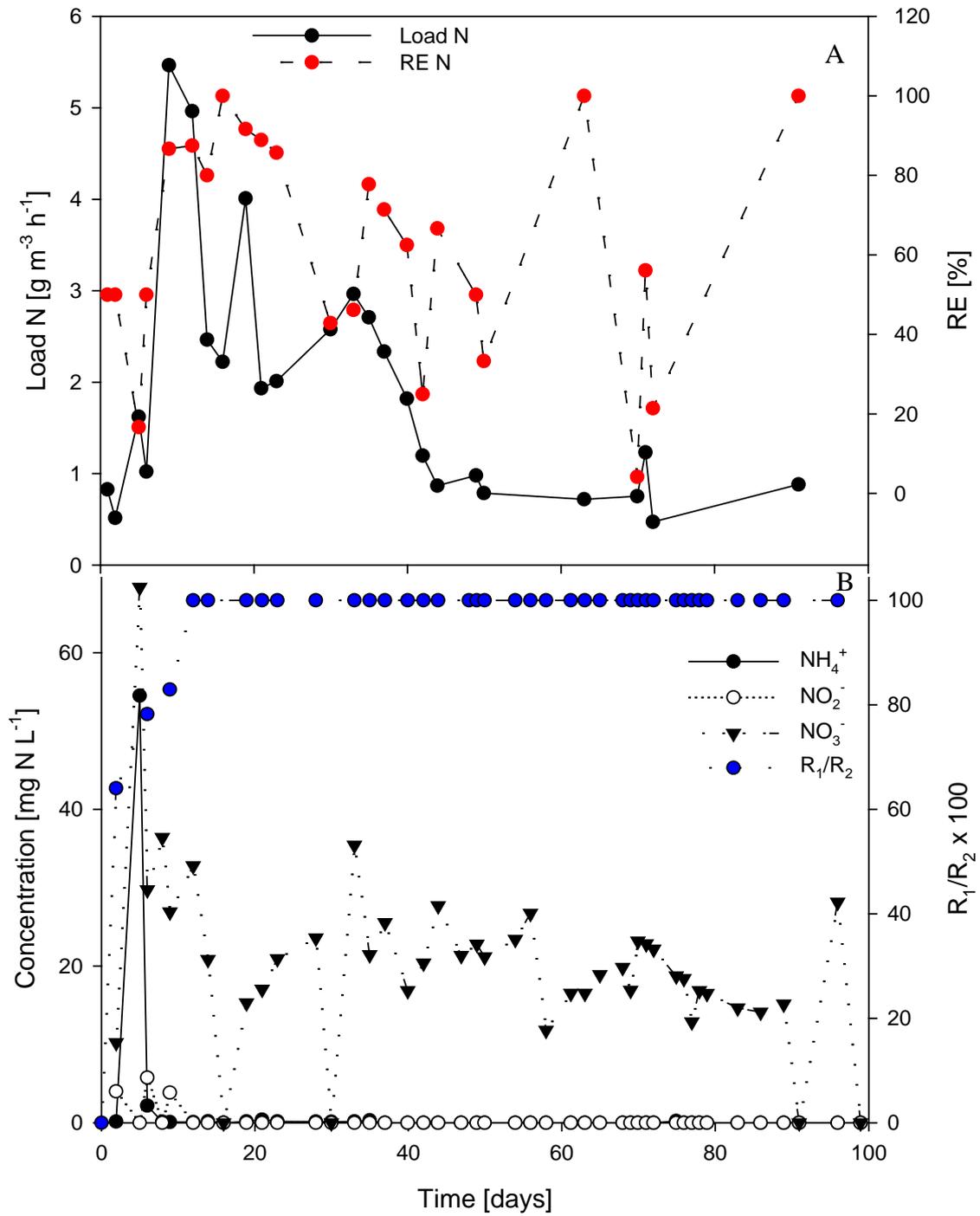


3

1

Figure 5

2



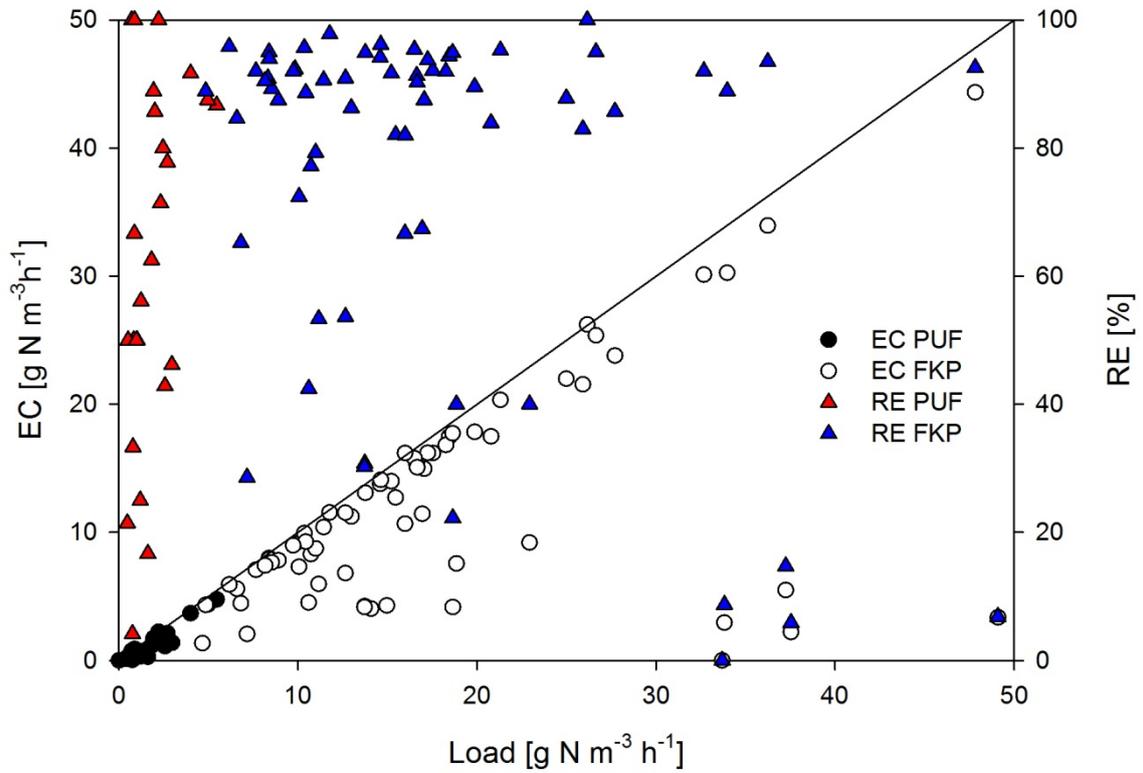
3

4

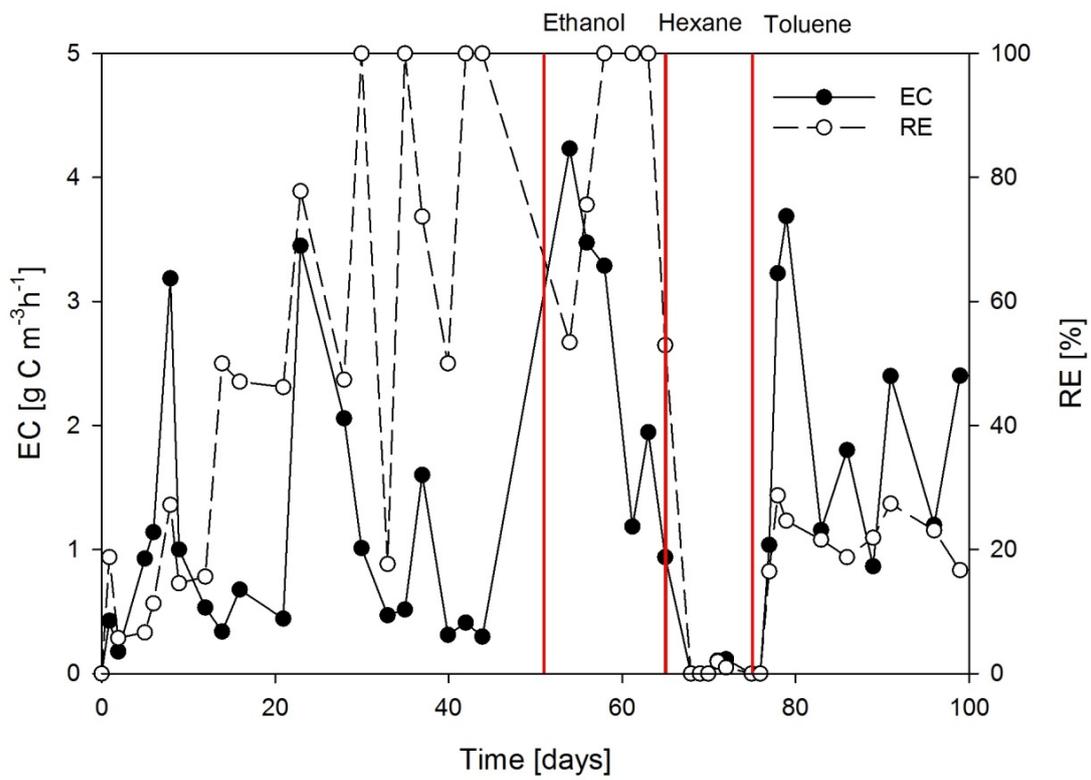
1

2

Figure 6



3



4

5

1 Table 1: Main operation conditions of the both support media

2

Packing material	Structured material	Unstructured material
Start of operation	12 th April	5 th October
End of operation	28 th July	12 th January
NH₃ inlet concentration (ppm_v)	13 – 89 (38*)	0 – 16 (4*)
VOCs inlet concentration (ppm_v)	0 – 133 (10*)	0 – 15 (5*)
Gas flowrate (m³ h⁻¹)	181 – 1272 (421*)	176 – 353 (251*)
Start of spiking	5 th July (day 84)	25 th November (day 51)
End of spiking	28 th July (day 107)	12 th January (day 99)

3

(*) average values

1
2 **BIOFILTRATION OF WWTP SLUDGE COMPOSTING EMISSIONS AT**
3 **CONTACT TIMES OF 2 TO 10 SEC BY UN/STRUCTURED PACKING**
4 **MATERIALS**

5
6 Antonio D. Dorado*, David Gabriel ** and Xavier Gamisans*

7 *Department of Mining Engineering and Natural Resources, Universitat Politècnica de Catalunya, Bases
8 de Manresa 61-73, 08240 Manresa, Spain

9 **Department of Chemical Engineering, Universitat Autònoma de Barcelona, Edifici Q, 08193
10 Bellaterra, Barcelona, Spain
11 E-mail: toni.dorado@upc.edu

12
13
14 **SUPPLEMENTARY CONTENT**
15
16



17
18 *Figure 1S. Images of the FKP 158 packing material.*
19



Figure 2S. Images of the PUF packing material.

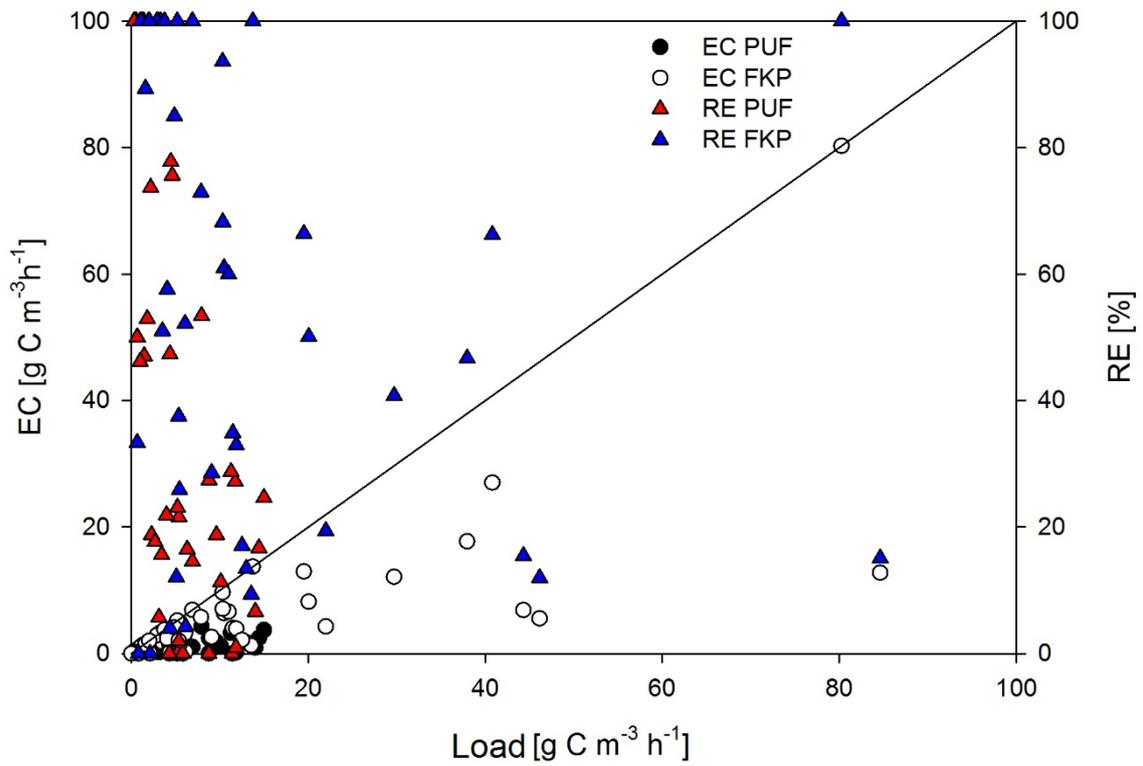


Figure 3S: Comparison of VOCs elimination capacities for PUF and FKP versus the inlet load.