

Non-thermal plasma assisting the biofiltration of volatile organic compounds

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1 **Abstract:** Unsteady loading rates can affect the proper operation of a biofilter. In addition,
2 biofiltration is known to be less effective when dealing with poorly soluble substances, like some
3 volatile organic compounds (VOCs). A non-thermal plasma (NTP) produced with a dielectric
4 barrier discharge (DBD) was studied as an option to pre-treat an air stream contaminated by a
5 mixture of VOCs. Therefore, the plasma reactor was operated upstream of a laboratory-scale
6 biofilter. Air admixed with toluene, *n*-heptane, *p*-xylene, ethylbenzene and benzene with average
7 concentrations of 95.6, 49.4, 60.8, 47.3 and 36.6 ppm, respectively, was used as a model polluted
8 gas, as these contaminants represent the air stripped by an oil-refinery wastewater treatment plant.
9 Peaks of loading rates at the inlet of the biofilter were simulated by the increase of the flow rates of
10 VOCs. The operation of NTP, with specific energy densities between 92 J·L⁻¹ and 256 J·L⁻¹ allowed
11 reducing the VOC concentrations down to the level of optimal biofilter operation. In addition, non-
12 water soluble VOCs were converted to more soluble compounds by the plasma treatment. In this
13 first attempt to investigate the synergies between NTP and biofiltration, NTP reveals as a promising
14 option to pre-treat effluents upstream of biofilters for optimized operation.

15

16 **Keywords:** dielectric barrier discharge; biofilter; air pollution control; industrial wastewater;
17 loading rate; BTEX.

18

19 **Nomenclature**

20 NTP: non-thermal plasma

21 DBD: dielectric barrier discharge

22 RH: relative humidity [%]

23 ΔP : pressure drop [mmH₂O]

24 EBRT: empty bed residence time [s]

25 SL: surface loading rate [m³·m⁻²·h⁻¹]

26 ML: mass loading rate [$\text{g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$]

27 RE: removal efficiency [%]

28 EC: elimination capacity [$\text{g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$]

29 SED: specific energy density [$\text{J}\cdot\text{L}^{-1}$]

30 EY: energy yield [$\text{g}\cdot(\text{kWh})^{-1}$]

31 P: discharge power [W]

32 C_{in} : inlet concentration [ppm]

33 M: molar mass [$\text{g}\cdot\text{mol}^{-1}$]

34 V_{m} : molar volume [$\text{L}\cdot\text{mol}^{-1}$]

35 EC_{max} : maximum EC [$\text{g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$]

36 EY_{max} : maximum EY [$\text{g}\cdot(\text{kWh})^{-1}$]

37 RE_{NTP} : RE of the NTP unit [%]

38 $RE_{\text{NTP,max}}$: maximum RE_{NTP} [%]

39

40 **Amount of words:** 6630

41

42 **1. Introduction**

43 Volatile organic compounds (VOCs) are air pollutants that originates both from natural sources
44 (*e.g.*, forest fires, deciduous trees) and from several types of anthropogenic activities, such as
45 transportation, usage and production of solvents, oil refineries, chemical industry, agriculture, gas
46 leakage from waste landfills and waste treatments (Derwent, 1995). A 56% decrease in VOC
47 emissions have been observed in Europe between 1990 and 2010 (European Environmental
48 Agency, 2012), due to improved air pollution control technologies and energy efficiency in the
49 transportation sector, which were also driven by more restrictive emission standards. The
50 contribution from other sectors remained substantially stable during this period. The joint

51 contributions of VOCs from industrial processes and the waste sector accounted for 8% of the total
52 VOC emissions in 2010 (European Environmental Agency, 2012). Industrial sites are generally
53 equipped with wastewater treatment plants (WWTPs) to recycle process water or wastewater and/or
54 purify it before its release into the environment (Deshmukh et al., 2015). Industrial WWTPs are
55 known sources of fugitive emissions of VOCs (Cunningham, 1995). Oil-refinery WWTPs, in
56 particular, are important contributors of aromatics and, more specifically, benzene, toluene,
57 ethylbenzene and xylene, also referred to as BTEX (Wei et al., 2014). Due to their volatilization,
58 VOCs are released from wastewater and are dispersed within the atmosphere (Fatone et al., 2011).
59 Here VOCs produce adverse effects to the environment, since they are promoters of tropospheric
60 ozone (O₃) and contribute to the formation of radicals and aerosols (Schiavon et al., 2016). At a
61 local scale, VOCs can have adverse effects on humans by inhalation, both in terms of nuisance (due
62 to their odor impact) and, especially, in terms of risks for health (Peishi et al., 2004; Civan et al.,
63 2015; Ni et al., 2015). Indeed, some VOCs are carcinogens for humans. Thus, long-term exposure
64 to VOCs in ambient air may induce the risk of cancer both in workers and in the populations settled
65 in the vicinity of VOC emission sources.

66 To reduce VOC releases from industrial WWTPs, the air of the different compartments is aspirated
67 and treated before being released to the atmosphere. The traditional technologies for the removal of
68 VOCs from air streams are based on physical-chemical methods, such as activated carbon
69 adsorption, thermal or catalytic incineration and chemical scrubbing (Tan, 2014; Schnelle et al.,
70 2016). However, such methods revealed to be unsuitable for the treatment of large air flows at
71 relatively low concentration of contaminants (< 100 ppm), due to their impacts in terms of material
72 and chemicals required, energy consumption, generation of waste products and related costs
73 (Fridman, 2008). The current solution to this issue is represented by biological technologies for air
74 pollution control. During the last decades, VOC removal and odor control at the outlet of
75 mechanical-biological treatments of waste or wastewater treatments have been successfully

76 achieved through biofiltration (Cabrera et al., 2011). In the so-called biofilters, the air flows through
77 a filtering bed. The pollutant molecules transfer into a thin biofilm that develops on the surface of
78 the packing material. Microorganisms, such as bacteria and fungi, are immobilized in the biofilm.
79 They capture and biologically degrade the pollutant molecules. Biofilters still represent the most
80 convenient method to treat the stripped air from WWTPs (Dorado et al., 2015). However, biological
81 technologies are susceptible to unsteady conditions of flow rate and pollutant concentration (Elías et
82 al., 2010), negatively influencing the adaptation time of the microorganisms (Ragazzi et al., 2014).
83 Peaks of concentrations may also cause shock to the microorganisms responsible of biodegradation
84 and this can affect the proper operation of the biofilter. In addition, the biodegradation of
85 hydrophobic compounds is problematic, because of the limited diffusion of pollutants from the
86 gaseous phase to the biofilm.

87 Activated carbon adsorption has been traditionally adopted as an equalization system to ensure
88 constant mass loading rate to biofilters. However, adsorption requires periodical replacement or
89 regeneration of the activated carbon. Therefore, a double activated carbon bed should be used to
90 ensure loading rate equalization during maintenance period of one bed, and this implies larger space
91 availability. In addition, adsorption cannot help biodegradation, since the contaminants are not
92 converted into more soluble compounds. Flow equalization may also be achieved with absorption
93 columns. However, a waste flow is formed, with additional costs for disposal.

94 A possible solution to these typical drawbacks of biological technologies for air pollution control
95 consists in pre-treating the gaseous effluent with a dual purpose: removing part of the inlet mass
96 load (in the case of peaks of concentrations and/or airflow rate) and increasing the solubility of the
97 mixture of incoming pollutants. A technology based on the generation of non-thermal plasma (NTP)
98 may help to achieve both these targets, as demonstrated in recent laboratory experiments:
99 Brandenburg et al. (2014) achieved satisfying results in the removal of hydrocarbons from air and in
100 the formation of water-soluble byproducts like formic acid after application of NTPs; Schiavon et

101 al. (2015), converted three VOCs in air to carbon monoxide (CO), carbon dioxide (CO₂) and minor
102 organic byproducts that were more water-soluble than the VOCs in the starting mixture.

103 In a recent work (Stasiulaitiene et al., 2016), through a comparative life-cycle assessment, the
104 authors concluded that NTP merits gaining consideration against traditional methods for air
105 pollution control, especially for its considerable lower impacts on health and environment. NTP for
106 air pollution control and, especially, VOC and odor removal has been the object of laboratory-scale
107 studies as well as in industrial installations. Several studies were carried out on the application of
108 NTP to remove single VOCs from air: Ye et al. (2008) adopted a dielectric barrier discharge (DBD)
109 to remove benzene from air, both a laboratory scale and at pilot scale; Schiorlin et al. (2009) applied
110 different kinds of corona discharges to abate toluene in air, providing possible mechanisms of
111 oxidation; Ragazzi et al. (2014) removed methyl ethyl ketone from dry synthetic air by applying a
112 DBD in a closed hydraulic circuit; Schmidt et al. (2015) adopted a DBD reactor to remove toluene
113 both from dry and wet synthetic air.

114 Less frequently, studies on VOC removal with NTPs were carried out on mixtures of compounds:
115 Kim et al. (2007) applied a plasma-driven catalysis (PDC) system, both as a flow-type reactor and
116 as a closed circuit, to remove a mixture of benzene and toluene from air; Subrahmanyam et al.
117 (2007) worked on a PDC system based on a DBD to remove toluene, isopropanol and
118 trichloroethylene from air by testing different catalysts; Schiavon et al. (2015) applied a DBD to
119 remove two mixtures of VOCs: ethanol and ethyl acetate, in a first experiment, and toluene,
120 benzene and *n*-octane in another experiment.

121 Only recently, fewer studies have investigated the combination of NTPs with biological
122 technologies for air pollution control. Wei et al. (2013) applied a biotrickling filter to remove the
123 residual dimethyl sulfide and the byproducts formed after applying a NTP to a mixture of dimethyl
124 sulfide and compressed air; Hofub et al. (2014) applied a NTP to ambient air, in order to generate

125 O₃, which was only used to treat part of the flow coming from the stripping air of a WWTP and, in
126 an alternative configuration, the effluent from a biofilter.

127 An investigation of the effects of an NTP pre-treatment on the biodegradation of VOCs is still
128 lacking. This paper focuses on a laboratory-scale study that aims at investigating possible
129 synergistic effects of NTP treatment and biofiltration in removing or converting a mixture of VOCs
130 from air. Therefore, a mixture of five VOCs was chosen to represent the stripping air of an
131 industrial WWTP. After completion of the startup phase of a laboratory-scale biofilter, a DBD
132 reactor was installed prior to the biofilter. It was studied whether the NTP treatment is able to
133 manage peaks of the inlet mass loading of pollutants, which often occur in real cases.

134

135 **2. Material and methods**

136 *2.1 Selection of the VOC mixture*

137 Five VOCs in total were chosen with the intention to represent a typical effluent stripped from the
138 wastewater of a petrochemical industry rather than to study the specifics of plasma chemistry.
139 Toluene, *n*-heptane, *p*-xylene, ethylbenzene and benzene were the most abundant VOCs measured
140 in the emissions from an existing industrial wastewater treatment plant located in Sicily (Italy). In
141 addition to the previously mentioned impacts of VOCs released into the atmosphere, benzene and
142 ethylbenzene are particularly important also from a toxicological point of view, since they are
143 carcinogenic compounds. The International Agency for Research on Cancer (IARC) classifies
144 benzene as a demonstrated carcinogen for humans (Group 1) and ethylbenzene as a possible
145 carcinogen to humans (Group 2B) (IARC, 2016). Thus, assuring a proper operation of a biofilter
146 subject to unsteady flow conditions reveals essential to limit human exposure by inhalation and the
147 consequent cancer risk in the population settled in the vicinity of an industrial wastewater treatment
148 plant.

149 All the substances were purchased as liquids from Sigma Aldrich Co. (USA). Toluene and benzene
150 have a purity $\geq 99.9\%$, while the purity of the other three compounds is $\geq 99.0\%$.

151

152 *2.2 Experimental setup*

153 The experimental setup consists in four main parts:

154 - five bubblers for the generation of vapor-phase VOCs and one bubbler containing demineralized
155 water for defined humidification of the air flow;

156 - the NTP unit, energized with a programmable AC source (61604, Chroma, USA) and a high-
157 voltage transformer. The electrical operational parameters were recorded using a digital
158 oscilloscope (DPO4104, Tektronix, USA) connected to a high-voltage probe (P6015A, Tektronix,
159 USA) and a 100 nF capacitor for voltage and charge measurements;

160 - the biofilter, manufactured by AirClean Srl (Italy);

161 - the analytical setup, composed of a Fourier-Transform-Infrared (FTIR) spectrometer (Antaris IGS
162 Analyzer, Thermo Scientific, USA), a gas-chromatograph (GC) (7890B, Agilent Technologies,
163 USA) coupled with a single quadrupole mass spectrometer detector (MS) (5977A MSD, Agilent
164 Technologies, USA) and a Micro-GC (3000 Micro GC, Inficon, Germany).

165 A scheme of the experimental setup is presented in Figure 1.

166

167 (Figure 1 should be placed here)

168

169 The five bubblers containing VOCs were fed with nitrogen (N_2) and each flow rate was adjusted till
170 obtaining the desired inlet concentrations of VOCs. Two flows of compressed air were used to
171 generate the main air flow: the first one was mixed with the five N_2 flows containing VOCs and its
172 airflow rate was kept at $62\text{--}71\text{ L}\cdot\text{h}^{-1}$; the second flow was made passing through the bubbler
173 containing demineralized water and its flow rate was kept at $79\text{--}88\text{ L}\cdot\text{h}^{-1}$; the two flows were

174 adjusted in order to generate a total air flow rate of $150 \text{ L}\cdot\text{h}^{-1}$ with a relative humidity (RH) of about
175 50%. Each single air flow was adjusted day by day, due to the outdoor temperature variation,
176 slightly influencing the temperature of the incoming compressed air. The choice of working with a
177 humid flow rate is motivated by the conditions in real applications. Dry flow conditions are unlikely
178 to occur when stripping air from wastewater. On the other hand, working with $\text{RH} > 50\%$ would not
179 allow correctly quantifying the discharge power of the NTP unit. The relative humidity and the
180 temperature of the inlet airflow were measured by means of a portable thermo-hygrometer (HP-
181 22A, Rotronic, Switzerland). The pressure drop (ΔP) between the inlet and the outlet of the biofilter
182 was kept under observation by two digital manometers (454 Data logger, Testo, Germany).

183

184 2.3 The biofilter

185 The laboratory-scale biofilter consists of a cylinder made of transparent polyvinyl chloride
186 (PVC), with internal diameter of 0.08 m and height of 0.80 m. The biofilter was filled with a
187 specialized patented peat (Mónafil[®], Bord Na Móna PLC, Ireland), till reaching a total filling height
188 of 0.50 m. The incoming air flow enters the biofilter from the bottom, passes through the bed
189 material and leaves the biofilter at the top outlet. The filling material is supported by a grid, placed
190 at 0.10 m from the bottom of the biofilter, favoring the contact between air and peat. The concepts
191 of empty bed residence time (EBRT, *i.e.*, the empty bed biofilter volume divided by the airflow
192 rate), surface loading rate (SL, *i.e.*, the airflow rate normalized to the area of the transversal section
193 of the bed) and mass loading rate (ML, *i.e.*, the mass flow rate per unit volume of the biofilter bed)
194 turns useful to contextualize the experiments and facilitate future comparisons with other studies on
195 laboratory-scale biofilters. At the flow rate investigated in this study ($150 \text{ L}\cdot\text{h}^{-1}$), EBRT and SL are
196 60 s and $29.8 \text{ m}^3\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, respectively. The performance of a biofilter is usually evaluated by means
197 of the concepts of removal efficiency (RE) and elimination capacity (EC, *i.e.*, difference between
198 incoming and outgoing mass flows).

199 Before inserting the filling material into the biofilter, the peat was mixed with a small amount of
200 lyophilized microbial inoculum (Air Clean Srl, Italy). The inoculum consists of a mixture of aerobic
201 bacteria, cultivated after extraction from the filling material of a former biofilter degrading VOCs
202 and odorants.

203

204 *2.4 The DBD*

205 The NTP unit is composed of a single-stack DBD reactor (Müller and Zahn, 2007). The high-
206 voltage and the ground electrodes are both made of a stainless-steel mesh, while the dielectric
207 consists of a layer of mica with a thickness of 0.5 mm. The reactor is enclosed in a volume of
208 250 mL, providing a residence time of 6 s at the flow rate investigated in this study. Along with RE,
209 the concepts of specific energy density (SED) and energy yield (EY) are used to assess the
210 performance of NTP in removing air pollutants. SED and EY are defined as follows:

$$SED = \frac{P}{Q} \quad (1)$$

$$EY = \frac{C_{in} \cdot RE \cdot M}{SED \cdot V_m} \quad (2)$$

211 where P is the discharge power (W), calculated through integration of the area of the voltage-charge
212 plots measured by electrical measurements and computed by the oscilloscope. Q is the airflow rate
213 ($L \cdot h^{-1}$), C_{in} is the inlet concentration (ppm), M is the molar mass of the compound ($g \cdot mol^{-1}$), V_m is
214 the molar volume, which at standard conditions (293 K and 101,325 Pa) is $24.04 L \cdot mol^{-1}$. SED and
215 EY are expressed as $J \cdot L^{-1}$ and $g \cdot (kWh)^{-1}$, respectively.

216

217 *2.5 Analytical setup*

218 The experimental setup was built in order to allow a complete characterization of the VOC/air
219 mixture prior to the NTP unit (sampling point A), between the NTP unit and the biofilter (sampling
220 point B) and downstream of the biofilter (sampling point C) (Figure 1). Through proper regulation

221 of the valves composing the system, the flow of interest passes through the FTIR first, subsequently
222 flows to the GC-MS and the Micro-GC, and is finally sent out to an exhaust aspiration system. The
223 FTIR was used to quantify CO, CO₂ and the O₃ generated by the DBD; the Micro-GC was used to
224 quantify each of the five VOCs; the byproducts of the DBD treatment were identified with the GC-
225 MS. The Micro-GC was calibrated with cylinder gases containing dry synthetic air (20% O₂ and
226 80% N₂) and the five components of the VOC mixture under investigation, at reference
227 concentrations. The mixture was purchased from Air Liquide (France). The FTIR, previously
228 calibrated for CO and CO₂, was also calibrated for O₃, through an ozonizer and subsequent
229 comparison between the areas of the O₃ peaks measured on the FTIR and the O₃ concentrations
230 measured by an O₃ monitor (Ozomat MP, Anseros, Germany). The pH of the filling material and of
231 the water collected at the bottom of the biofilter was measured by means of the Litmus test.
232 Microbiological analyses were also carried out on samples of filling material, in order to assess the
233 vitality and the type of the microorganisms involved in VOC biodegradation.

234

235 *2.6 Biofilter startup*

236 To allow for a proper growth of the bacteria initially present in the inoculum, biofilters require a
237 startup phase of several weeks. During this phase, ML is gradually increased till reaching stable
238 removal performance. In this study, the initial VOC concentrations were increased at the design air
239 flow rate (150 L·h⁻¹). The biofilter was initially fed with only toluene, starting from a concentration
240 of about 30 ppm. The biofilter was daily monitored and, every time the biofilter reached a
241 RE > 90%, the initial concentration was subsequently increased till reaching a target concentration.
242 Afterwards, a new compound was added to the mixture and the same procedure was followed with
243 the remaining VOCs. During the startup phase, the air temperature remained comprised between
244 24.0 and 25.6 °C.

245 At the end of the startup phase, the average concentrations of the single VOCs at the inlet of the
246 biofilter resulted as 95.6 ppm of toluene, 49.4 ppm of *n*-heptane, 60.8 ppm of *p*-xylene, 47.3 ppm of
247 ethylbenzene and 36.6 ppm of benzene.

248 A proper humidification of the filtering medium was assured by the partially humidified air flow
249 and by regular addition of 100 mL of water every 72 h. After completion of the startup phase, this
250 interval was increased to 96 h. Except from water, no nutrient solution was added to the biofilter
251 during the whole period.

252

253 *2.7 Experimental procedure*

254 After the completion of the startup phase, the airflow rate was kept constant at 150 L·h⁻¹ and the
255 inlet VOC concentrations were kept as close as possible to the reference average concentrations
256 reported above.

257 To test the application of NTP on emission peaks of VOCs and, meanwhile, not to stress the
258 microorganisms in the biofilter, the following test procedure was implemented. The rates of the N₂
259 gas flows feeding the bubblers were increased by 25%; the VOC concentrations in the air flow
260 consequently increased; the NTP was switched on and the energy provided to the discharge was
261 gradually increased to the energy necessary to obtain again the initial total concentration of the five
262 starting VOCs (about 290 ppm) at the inlet of the biofilter. This way, the DBD can be studied as a
263 pre-treatment module to reduce peaks of concentrations and to level the concentrations in the flow
264 exiting the DBD to the values the biofilter was acclimated at. Keeping the concentrations constant
265 at the inlet of the biofilter would preserve microorganisms from shock, would allow a proper
266 operation of the biofilter and would not negatively affect its RE. Meanwhile, the efficiency and the
267 energy consumption of the DBD can be tested.

268 After carrying out these tests, the same procedure was repeated with increasing the rates of the N₂
269 flows feeding the bubblers containing VOCs by 50% and 100%. All the errors were determined by
270 the error propagation formula, considering the instrumental and calibration errors.

271

272 **3. Results and discussion**

273 *3.1 Biofilter startup*

274 Four days after the startup of the biofilter, the RE of toluene became close to 90%, so that its
275 concentration at the inlet of the biofilter was increased to about 70 ppm. After 9 d of operation, the
276 biofilter was capable to degrade toluene at its target concentration (95.6 ppm) with a 99% RE.
277 Afterwards, *n*-heptane was inserted into the mixture at an initial concentration of 25 ppm. 25 d later,
278 a 99% RE was obtained and, then, its inlet concentration was increased to the reference average
279 value (49.4 ppm). *p*-Xylene, ethylbenzene and benzene were added to the system one by one, after
280 that REs > 99% had been reached with regards to every new VOC introduced. The acclimation
281 period of the microorganisms to these three VOCs was particularly short: indeed, after a total time
282 of 30 d of operation, the biofilter became fully operative and the RE was > 99% for all the VOCs in
283 the mixture, with the only exception of *n*-heptane. The inlet VOC concentrations and their RE
284 values during the startup phase of the biofilter are reported in Figure 2. Microbiological analyses on
285 samples of peat revealed that the microorganisms present in the filling material belonged to the
286 *Pseudomonas* and *Bacillus* strains. The cell count at the end of the startup phase resulted in
287 3.95×10^5 CFU·g⁻¹ of dry material. During the whole period of operation of the biofilter, the
288 maximal ΔP between B and C resulted in 40 mmH₂O.

289

290 (Figure 2 should be placed here)

291

292 *3.2 Application of NTP*

293 After increasing the N₂ flow rates of every VOC line by 25%, 50% and 100%, the inlet VOC
294 concentrations changed to the values reported in Table 1. The SED provided to the DBD reactor
295 was gradually increased from 46 J·L⁻¹ to 128 J·L⁻¹, from 49 J·L⁻¹ to 165 J·L⁻¹ and from 92 J·L⁻¹ to
296 256 J·L⁻¹, in the case of a 25%, 50% and 100% increase of N₂ flow rates, respectively. With every
297 increase in the power provided to the DBD, the VOC concentrations were continuously monitored
298 both at the sampling point B and at the sampling point C, in order to assess both the performance of
299 the only NTP treatment and of the NTP-biofilter combined system. The VOC concentrations at the
300 outlet of the NTP unit (B), at the different SED values investigated, are reported in Figure 3.
301 Hereinafter, for an easier view of the graphs, the errors associated with the SED (estimated as equal
302 to 10% of the value) are not shown.

303

304 (Table 1 should be placed here)

305

306 (Figure 3 should be placed here)

307

308 As expected, the VOC concentrations decrease with the increase of SED due to the conversion of
309 the initial compounds by plasma chemical reactions. However, a threshold SED of 70–125 J·L⁻¹ can
310 be observed before a significant removal can be obtained. This can be explained by the presence of
311 humidity in the airflow, *i.e.*, a part of the energy provided to the DBD is dissipated through
312 excitation of the vibrational levels and polarization of water molecules instead of formation of
313 reactive species for VOC conversion.

314 The VOC showing the smallest degradation of all VOCs is benzene, which seems to be even
315 reformed at a SED comprised between 95 J·L⁻¹ (in the case of a 25% increase of the N₂ flow rates
316 feeding the bubblers containing the initial VOCs) and 125 J·L⁻¹ (in the case of a 100% increase).
317 This is consistent with the results of a former experiment (Schiavon et al., 2015) on toluene,

318 benzene and *n*-octane, in which the reformation of benzene was ascribed to toluene degradation
319 operated by NTP. The formation of benzene was also reported by Huang et al. (2011) after
320 treatment of gaseous toluene in humid air with a PDC system. At the maximal SED values
321 investigated, the concentrations of every VOC at the inlet of the biofilter (B) are close to the inlet
322 concentrations achieved at the end of the startup phase, thus before any tests with plasma.

323 Trace concentrations of benzaldehyde, acetophenone, styrene and formic acid were detected in the
324 effluent from the DBD reactor, as the main organic byproducts of the NTP degradation of the VOCs
325 initially present in the mixture. At increasing SED, the formation of such byproducts is more and
326 more reduced. All the byproducts formed are more water-soluble than the initial VOCs. These
327 results are in line with a previous study, in which a mixture of benzene, toluene and *n*-octane was
328 converted to CO₂, CO and to more water-soluble trace VOCs like benzaldehyde, phenol, benzyl
329 alcohol, benzyloxy-benzene, cresols and isomers of octanedione (Schiavon et al., 2015). In addition,
330 at the outlet of the NTP unit, the carcinogenic potential of the mixture is reduced, since it is related
331 only to residual benzene and ethylbenzene, and to traces of styrene (generated by the application of
332 NTP), classified in the Group 2B by the IARC (IARC, 2016) and not classified as a carcinogen by
333 the United States Environmental Protection Agency (USEPA, 2016). The remaining organic
334 byproducts (benzaldehyde, acetophenone and formic acid) are not carcinogenic to humans. USEPA
335 provides a “no observed adverse effect level” (NOAEL) of 10,000 ppm for acetophenone and only
336 an oral reference dose value for benzaldehyde (USEPA, 2017). No NOAEL or reference
337 concentration value is available for formic acid. NTP generated a maximal O₃ concentration of
338 250 ppm, which is considered tolerable by microbial populations, as reported by Wang et al. (2013),
339 who injected O₃ in a membrane bioreactor at a concentration of about 280 ppm with no observed
340 adverse effects on the microbial populations. The maximal CO₂ concentrations generated by NTP
341 were achieved at the maximal SED applied, and varied between 333 and 840 ppm in the case of a
342 25% and a 100% increase in the VOC flow rates, respectively. The DBD also generated maximal

343 CO concentrations of 227 and 504 ppm, after increasing the VOC flow rates by 25% and 100%,
344 respectively.

345 The overall RE values of the five initial VOCs after the combined NTP-biofilter treatments
346 (sampling point C) at increased VOC concentrations are presented in Figure 4 as a function of the
347 SED. At the maximal SED values (128, 165 and 256 J·L⁻¹, in the case of a 25%, 50% and 100%
348 increase in the N₂ flow rates, respectively), the RE values of the initial VOCs were > 93%, with the
349 only exception of *n*-heptane, whose maximal RE varied in the range 81–91%, the lowest value
350 being referred to the case with a 100% increase in the VOC flow rates. Such value is in good
351 agreement with the RE of *n*-heptane obtained only with the biofilter and before increasing the initial
352 VOC concentrations. To confirm that the biofilter alone would have not been able to ensure
353 satisfying RE values after increasing the ML of the five VOCs, the RE of the biofilter was
354 investigated after switching off the DBD (*i.e.*, SED = 0 J·L⁻¹), at the end of the test with N₂ flow
355 rates increased by 100%, before lowering the VOC concentrations to the initial values. Under these
356 conditions, the RE values of toluene, *n*-heptane, *p*-xylene, ethylbenzene and benzene were
357 significantly reduced, namely at 60%, 23%, 87%, 76% and 28%, respectively.

358

359 (Figure 4 should be placed here)

360

361 The CO concentration at the outlet of the biofilter was up to 10% lower than its concentration after
362 the NTP unit. This suggests that part of CO, toxic to several bacterial strains, may have been
363 metabolized by the microorganisms, with possible poisoning. The cell count at the end of all the
364 tests with NTP resulted in 2.95×10^5 CFU·g⁻¹ of dry material, *i.e.*, 25% lower than the value
365 measured at the end of the startup phase of the biofilter. At the present state, CO production
366 represents an important drawback of the application of NTPs as a pre-treatment of biofiltration.
367 Such limitation requires further research in view of upscaling this technology to pilot and real

368 scales. As a solution to this possible criticality, CO could be treated in a first biofilter stage
369 inoculated with CO-degrading populations under aerobic conditions, *e.g.*, the *Pseudomonas*
370 *carboxydovorans* (Meyer and Schlegel, 1978). However, such decrease in the cell count might also
371 be attributed to two additional causes: the temporary unavoidable stress to bacteria during the
372 transient phase between the concentration increases and the adjustment of the NTP unit to reach
373 optimal removal conditions; the absence of micronutrients supplied to the microorganisms.

374 The maximal EC (EC_{max}) of the five initial VOCs during each of the three tests are reported in
375 Table 2 together with the respective SED and ML values. Since the tests were carried out by
376 gradually increasing the SED with the aim of achieving satisfying overall RE, EC_{max} increases with
377 increasing the ML. In the case of toluene and benzene, after a 25% and 50% increase in the N₂ flow
378 rates, EC_{max} was achieved with the biofilter alone, which assured almost complete removal of these
379 compounds. The highest EC_{max} values were achieved by toluene (24.40, 37.75 and 49.02 g·m⁻³·h⁻¹
380 after increasing the N₂ flow rates by 25%, 50% and 100%, respectively), which is the most
381 concentrated VOC in the mixture. The lowest EC_{max} values were achieved by benzene (9.05, 10.37
382 and 13.72 g·m⁻³·h⁻¹ after increasing the N₂ flow rates by 25%, 50% and 100%, respectively), which
383 is the least concentrated VOC. Although the ML values of the remaining VOCs are similar, EC_{max}
384 increases when moving from *n*-heptane to ethylbenzene and, finally, to *p*-xylene.

385

386 (Table 2 should be placed here)

387

388 Table 3 presents the maximal EY (EY_{max}) obtained for each VOC after the NTP treatment, the
389 respective SED, the corresponding overall RE of the NTP-biofilter combined treatment, the
390 respective RE of the NTP treatment alone (RE_{NTP}) and the maximal RE of the NTP treatment alone
391 ($RE_{NTP,max}$) achieved within the range of SED investigated in each test with increased initial
392 concentrations. From the point of view of energy consumption, the most difficult compound to be

393 degraded by NTP is benzene, whose degradation requires more energy than the other VOCs in the
394 mixture. In analogy with EC_{\max} (Table 2), benzene is followed by *n*-heptane, ethylbenzene, *p*-
395 xylene and toluene, which gradually allow for higher EY.

396

397 (Table 3 should be placed here)

398

399 In general, the more the initial compounds are concentrated (*e.g.*, after a 100% increase in the N_2
400 flow rates), the higher EY_{\max} is. In fact, at higher initial concentrations, the probability of reaction
401 between O_3 and radicals with the initial compounds increases. Two exceptions are only for toluene
402 and benzene, whose EY_{\max} after a 50% increase of the N_2 flow rates is 5.29 and 1.12 $g \cdot kWh^{-1}$,
403 respectively, while the respective EY_{\max} reduces to 4.82 and 0.78 $g \cdot kWh^{-1}$ after a 100% increases of
404 the N_2 flow rates. The overall RE corresponding to EY_{\max} is always $> 92\%$, with the exception of *n*-
405 heptane, whose overall RE is equal to 89%, 84% and 81% when increasing the VOC flow rates by
406 25%, 50% and 100%, respectively.

407 NTP upscaling may be achieved by placing multiple stack reactors in parallel one to another.
408 Number and size of the stack reactors and their distance would depend on the characteristics of the
409 effluent (airflow rate and VOC concentration). It is expected that the results of a full-scale
410 application will be similar to those obtained at laboratory-scale, especially concerning byproduct
411 formation, if the inlet VOC mixture was the same. Energy consumption will be higher, but the use
412 of NTP would be limited to the abatement of peaks of concentrations that would destabilize the
413 biomass in a biofilter. Furthermore, NTPs would be a more flexible solution compared to traditional
414 buffer systems, since plasma can be activated and deactivated at every moment, with a consequent
415 energy and material saving.

416

417 **4. Conclusions**

418 This study presented a first investigation on the synergistic effects between NTP and biofiltration
419 for VOC removal. As a result of the tests carried out, NTP reveals as a promising technology to pre-
420 treat a VOC-containing effluent during increases in the ML that compromise the proper operation of
421 a biofilter. Satisfying overall RE values were obtained with relatively low energy consumption,
422 since the maximal SED used was $256 \text{ J}\cdot\text{L}^{-1}$. Although performance parameters like EC_{max} and
423 EY_{max} are partially influenced by the initial VOC concentrations, a ranking of the VOCs most
424 difficult to be abated by NTP and by the combined NTP-biofilter system can be anyway drawn up.
425 Benzene resulted as the most energy-demanding and, in general, less degradable VOC, followed by
426 *n*-heptane, ethylbenzene, *p*-xylene and toluene. NTP helps to keep the concentrations constant at the
427 inlet of the biofilter (in spite of the increases in the concentrations induced on purpose), which can
428 be done on demand as the NTP needs no acclimation and is directly controlled by its electrical
429 operation parameters such as high voltage amplitude and frequency. Furthermore, it demonstrates to
430 be capable of generating byproducts that are more soluble in water than the initial VOCs and this
431 could further help the biodegradation. Finally, the byproducts formed during these tests are less
432 toxic than the initial VOCs. However, a 25% decrease in the microbial cell number was observed
433 during the tests, probably because of poisoning effects of the CO generated by the DBD, as well as
434 absence of nutrients for microorganisms and the stress to the microbial populations provoked during
435 the attempts to adjust the energy provided to the DBD till reaching satisfying RE. CO generation
436 represents the main limitation of an NTP-biofiltration combined system at the present state.

437 In view of future applications, appropriate solutions including the primary removal of the CO
438 generated by plasma, the supply of nutrients and the optimization of the adjustment of the NTP
439 settings should be pursued. In addition, further steps should include an understanding of the
440 mechanisms leading to the formation of the byproducts detected: the relatively high number of
441 initial VOCs (motivated by the intention to get as close as possible to real-world conditions)
442 complicates the identification of pathways of byproduct formation, which falls out of the topic of

443 this study (centered on innovative technologies for air cleaning purposes) and would deserve a
444 dedicated investigation in the field of plasma chemistry.

445

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455

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556

Figure captions

Figure 1: Configuration of the experimental setup (MFC: mass flow controller; MIX: mixing chamber; OSC: oscilloscope; HVT: high-voltage transformer; PPS: programmable power source).

Figure 2: Trends *a)* of the VOC concentrations at the inlet of the biofilter and *b)* of the respective RE values during the startup phase of the biofilter.

Figure 3: VOC concentrations measured at point B as a function of the SED during the tests with a *a)* 25%, *b)* 50% and *c)* 100% increase in the N₂ flow rates feeding the bubblers containing the VOCs.

Figure 4: Overall RE values of the five reference VOCs after the combined NTP-biofilter treatment with a *a)* 25%, *b)* 50% and *c)* 100% increase in the initial VOC concentrations.

Tables

Table 1: VOC concentrations (expressed as ppm) measured at the sampling point A, before and after each increase in the VOC flow rates.

		Toluene	<i>n</i>-Heptane	<i>p</i>-Xylene	Ethylbenzene	Benzene
25% increase	Before	101.0 ± 3.9	52.5 ± 1.9	68.3 ± 3.9	47.9 ± 2.7	39.4 ± 1.7
	After	125.7 ± 4.8	63.9 ± 2.3	85.1 ± 4.9	62.1 ± 3.6	47.3 ± 2.0
50% increase	Before	94.4 ± 3.6	48.3 ± 1.8	58.7 ± 3.4	46.1 ± 2.6	36.9 ± 1.6
	After	140.3 ± 5.4	71.0 ± 2.6	88.1 ± 5.0	73.4 ± 4.2	53.3 ± 2.3
100% increase	Before	91.3 ± 3.5	47.5 ± 1.7	55.4 ± 3.2	47.9 ± 2.7	33.6 ± 1.5
	After	182.3 ± 7.0	98.3 ± 3.6	126.5 ± 7.2	96.5 ± 5.5	70.3 ± 3.0

Table 2: EC_{max} of the biofilter and respective ML and SED values of the five reference VOCs achieved during the three tests with a 25%, 50% and 100% increase in the VOC flow rates (ML and EC_{max} are expressed as g·m⁻³·h⁻¹, SED is expressed as J·L⁻¹).

		25% increase	50% increase	100% increase
Toluene	EC _{max}	28.40 ± 1.09	31.69 ± 1.22	40.27 ± 1.55
	ML	28.40 ± 1.09	31.69 ± 1.22	41.18 ± 1.58
	SED	0 ± 0	0 ± 0	191 ± 10
<i>n</i>-Heptane	EC _{max}	14.30 ± 0.54	15.90 ± 0.59	16.95 ± 0.74
	ML	15.70 ± 0.58	17.43 ± 0.64	24.15 ± 0.89
	SED	111 ± 6	165 ± 8	191 ± 10
<i>p</i>-Xylene	EC _{max}	22.16 ± 1.27	22.93 ± 1.31	31.69 ± 1.82
	ML	22.16 ± 1.27	22.93 ± 1.31	32.91 ± 1.88
	SED	46 ± 2	123 ± 8	223 ± 11
Ethylbenzene	EC _{max}	16.16 ± 0.92	18.89 ± 1.08	23.21 ± 1.34
	ML	16.16 ± 0.92	19.09 ± 1.09	25.12 ± 1.44
	SED	74 ± 4	165 ± 8	191 ± 10
Benzene	EC _{max}	9.05 ± 0.39	10.20 ± 0.44	13.46 ± 0.58
	ML	9.05 ± 0.39	10.20 ± 0.44	13.46 ± 0.58
	SED	0 ± 0	0 ± 0	125 ± 6

Table 3: EY_{\max} and respective SED, overall RE, RE_{NTP} and $RE_{\text{NTP,max}}$ of the five reference VOCs obtained during the three tests with increased initial concentrations (EY_{\max} is expressed as $\text{g}\cdot\text{kWh}^{-1}$, SED in $\text{J}\cdot\text{L}^{-1}$ and RE values as a percentage).

		25% increase	50% increase	100% increase
Toluene	EY_{\max}	3.63 ± 0.87	5.29 ± 0.92	4.82 ± 0.78
	SED	111 ± 6	123 ± 6	191 ± 10
	overall RE	100.0 ± 0.0	100.0 ± 0.0	97.8 ± 0.1
	RE_{NTP}	23.7 ± 3.8	34.3 ± 3.3	37.3 ± 3.1
	$RE_{\text{NTP,max}}$	23.7 ± 3.8	42.4 ± 2.9	40.5 ± 3.0
<i>n</i>-Heptane	EY_{\max}	2.13 ± 0.43	3.17 ± 0.44	3.20 ± 0.47
	SED	128 ± 6	145 ± 7	191 ± 10
	overall RE	89.2 ± 0.5	84.4 ± 0.8	81.4 ± 0.9
	RE_{NTP}	28.9 ± 3.6	44.0 ± 2.8	42.2 ± 2.9
	$RE_{\text{NTP,max}}$	28.9 ± 3.6	45.5 ± 2.7	48.0 ± 2.6
<i>p</i>-Xylene	EY_{\max}	5.09 ± 1.14	5.39 ± 0.73	5.15 ± 1.09
	SED	74 ± 4	145 ± 7	148 ± 7
	overall RE	100.0 ± 0.0	96.7 ± 0.2	93.7 ± 0.5
	RE_{NTP}	28.4 ± 3.6	57.0 ± 2.2	38.6 ± 4.4
	$RE_{\text{NTP,max}}$	43.1 ± 2.8	59.4 ± 2.0	60.7 ± 2.8
Ethylbenzene	EY_{\max}	2.95 ± 1.19	3.95 ± 1.36	3.49 ± 0.56
	SED	46 ± 2	49 ± 2	191 ± 10
	overall RE	97.9 ± 0.1	96.6 ± 0.2	92.3 ± 0.4
	RE_{NTP}	14.0 ± 4.3	16.9 ± 4.2	44.1 ± 2.8
	$RE_{\text{NTP,max}}$	32.9 ± 3.4	51.5 ± 2.4	49.5 ± 2.5
Benzene	EY_{\max}	0.41 ± 0.26	1.12 ± 0.25	0.78 ± 0.18
	SED	111 ± 6	145 ± 7	256 ± 13
	overall RE	100.0 ± 0.0	92.8 ± 0.4	97.9 ± 0.1
	RE_{NTP}	8.2 ± 4.6	26.6 ± 3.7	24.6 ± 3.8
	$RE_{\text{NTP,max}}$	9.6 ± 4.5	26.6 ± 3.7	24.6 ± 3.8