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Title: Headspace needle-trap analysis of priority volatile organic compounds from aqueous samples: application to the analysis of natural and waste waters

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6 **Headspace needle-trap analysis of priority volatile**  
7 **organic compounds from aqueous samples: application**  
8 **to the analysis of natural and waste waters**

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16

17 **Abstract**

18 Combining headspace (HS) sampling with a needle-trap device (NTD) to determine  
19 priority volatile organic compounds (VOC's) in water samples results in improved  
20 sensitivity and efficiency when compared to conventional static HS sampling. A 22  
21 gauge stainless steel, 51-mm needle packed with Tenax TA and Carboxen 1000  
22 particles is used as the NTD. Three different HS-NTD sampling methodologies are  
23 evaluated and all give limits of detection for the target VOC's in the  $\text{ng}\cdot\text{L}^{-1}$  range.  
24 Active (purge-and-trap) HS-NTD sampling is found to give the best sensitivity but  
25 requires exhaustive control of the sampling conditions. The use of the NTD to collect  
26 the headspace gas sample results in a combined adsorption/desorption mechanism. The  
27 testing of different temperatures for the HS thermostating reveals a greater desorption  
28 effect when the sample is allowed to diffuse, whether passively or actively, through the  
29 sorbent particles. The limits of detection obtained in the simplest sampling  
30 methodology, static HS-NTD (5mL aqueous sample in 20 mL HS vials, thermostating  
31 at 50°C for 30 minutes with agitation), are sufficiently low as to permit its application to  
32 the analysis of 18 priority VOC's in natural and waste waters. In all cases compounds  
33 were detected below regulated levels.

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36 **Keywords:** needle-trap, headspace, wastewaters, adsorption, VOC

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38 **1. Introduction**

39 The contamination of water supplies is a growing cause of environmental and health  
40 concern. The US Environmental Protection Agency's (US-EPA) National Water  
41 Quality Inventory of 2004 [1] identified agriculture, atmospheric deposition,  
42 construction, habitat alteration, hydromodification, and industrial activity as the largest  
43 sources of pollutants in rivers, lakes, and estuaries in the United States. One of the most  
44 ubiquitous families of contaminants is volatile organic compounds (VOC's), which are  
45 emitted as gases from both anthropogenic and biogenic sources. Most of the health  
46 effects described for these compounds are not a result of low level exposure but are  
47 rather associated with occupational exposure, controlled laboratory experiments and  
48 substance abuse [2]. The ability to monitor VOC's at low levels in environmental  
49 waters will greatly facilitate the study of their possible effects on human health.

50 As VOC's are typically present at very low concentrations (i.e. in the range of  $\text{ng}\cdot\text{L}^{-1}$ ) in  
51 surface and ground waters, highly sensitive methods of determination are required. The  
52 most sensitive and common methodologies currently used for the analysis of VOC's in  
53 waters are based on the purge-and-trap (PT) technique [3,4] and solid phase  
54 microextraction (SPME) [5,6] and have detection limits in the range of hundreds of  
55  $\text{ng}\cdot\text{L}^{-1}$ . However, these detection limits are still too high for the accurate determination  
56 of VOC's in natural waters. A report by the US Geological Survey [7] showed that only  
57 in ~19% of the ground-water samples analyzed in aquifer studies (from 3,498 wells)  
58 was it possible to detect the presence of one or more VOC's at an assessment level of  
59  $200\text{ ng}\cdot\text{L}^{-1}$  but this increased to ~51% (from 1,687 wells) when a method with a  
60 detection limit of  $20\text{ ng}\cdot\text{L}^{-1}$  was used.

61 The current trend is to develop methods that are not only more sensitive, but which are  
62 also fast, reproducible, accurate, automated, environmentally friendly, and portable for  
63 on-site use [8,9]. In-tube or in-needle sorptive extraction methods are approaches based  
64 on dynamic headspace (HS) that have been developed to overcome the relatively limited  
65 concentration capacity of SPME [10]. Needle-trap devices (NTD's), summarized details  
66 of which can be found in several recent reviews [8,11-14], use blunt hypodermic  
67 needles packed with an appropriate sorbent and allow laboratory automation and on-site  
68 sampling as well as coupling to analytical instrumentation [14].

69 NTD's present different advantages: (i) robustness and adaptability to different  
70 sampling methodologies, (ii) simplicity and relatively low cost as no specific additional  
71 instrumentation is required, and (iii) a high level of efficiency and sensitivity enabling  
72 the detection of target VOC's at low  $\text{ng}\cdot\text{L}^{-1}$  levels with small sample volumes [15].

73 NTD's have mostly been used for the analysis of gaseous samples and their application  
74 to HS analysis of water is still limited. When used, HS sampling has typically been  
75 active (i.e. purge-and-trap) [9,16-18] although there are a few cases where it has been  
76 static [9,19,20]. In all these studies, benzene, toluene, ethylbenzene and xylenes  
77 (BTEX) were the target compounds and real samples were rarely evaluated [18-20].

78 In the present study we have evaluated and compared the behavior of NTD's for the  
79 analysis of 18 VOC's taken from the lists of priority pollutants given in the US Clean  
80 Water Act [21] and EU Directive [22] (Table 1). After evaluating four different  
81 sampling methods, the most appropriate sampling method is selected for the analysis of  
82 aqueous samples from three waste-water treatment plants (WWTP's) and some natural,  
83 mineral and tap waters.

84

## 85 **2. Experimental**

### 86 **2.1. Materials**

87 Carboxen 1000 (60/80 mesh, specific surface area of  $1200\text{ m}^2\cdot\text{g}^{-1}$  and a density of  $0.47$   
88  $\text{g}\cdot\text{mL}^{-1}$ ) and Tenax TA (60/80 mesh, specific surface area of  $35\text{ m}^2\cdot\text{g}^{-1}$  and a density of  
89  $0.25\text{ g}\cdot\text{mL}^{-1}$ ) were used as sorbent materials (Supelco, Bellefonte, PA, USA). Reagents  
90 (purity  $>97\%$ , Table 1) were supplied by Sigma-Aldrich (Steinheim, Germany).

91 22-gauge (22G, O.D. 0.71 mm, I.D. 0.41 mm, 51 mm length) stainless steel (metal hub)  
92 needles with point style 5 were from Hamilton (Bonaduz, Switzerland). Gold wire of  
93  $100\text{ }\mu\text{m}$  diameter (Supelco) was used to prepare the spiral plugs to hold the sorbent  
94 particles inside the needles. HS vials, Teflon/silicone septum and caps were purchased  
95 from Supelco.

96 Stock solutions were freshly prepared daily by spiking milli-Q water (Millipore Iberica,  
97 Barcelona, Spain) with  $50\text{ }\mu\text{L}$  of a methanolic solution containing the compounds at  
98  $320\text{-}590\text{ mg}\cdot\text{L}^{-1}$ . These solutions were transferred to HS vials, filling them to avoid any

99 remaining headspace. The vials were then closed and stored at 4°C. Working solutions  
100 were prepared by the appropriate dilution of the stock solution in milli-Q water. In order  
101 to prevent VOC loss during the preparation of the solutions and samples, glass syringes  
102 (Hamilton) were used for sample transfer taking care to avoid the formation of gas  
103 space in the syringes [23].

104

## 105 2.2. Sampling by needle-trap device

106 Each NTD was prepared by taking a 51-mm long, 22G, stainless steel needle and filling  
107 it with the sorbent materials (Figure 1). The following protocol was used to immobilize  
108 sorbent particles inside the needle [15]: (i) a small piece of spiral plug (five turns) was  
109 fixed in the tip of the needle to prevent sorbent particles from becoming fixed in the  
110 side hole of the needle; (ii) 20 mm of Tenax TA was aspirated first with the help of a  
111 vacuum pump and positioned in the tip of the needle, 10 mm of Carboxen 1000 was  
112 then fixed in the shaft to prevent low volatile compounds contacting the stronger  
113 sorbent, Carboxen, during the sorption and desorption processes, so avoiding memory  
114 effects [24]; (iii) another spiral plug was carefully introduced into the upper position of  
115 the needle until it reached the end of the Carboxen layer. Each NTD was conditioned in  
116 the GC injector at 300°C for 2-3 hours with a permanent helium flow to remove  
117 impurities. Finally, the tip end was sealed with the help of a Teflon septum and the  
118 upper part of the needle was closed with a push-button syringe valve (SGE Europe Ltd,  
119 Milton Keynes, UK) to prevent contamination during storage. This procedure avoids the  
120 use of epoxy resin, which leads to significant levels of impurities in ultra-trace analysis  
121 [15].

122 A preliminary study highlighted the importance of controlling sampling flow when  
123 using needle traps and found manual sampling to have significant limitations and to  
124 give poor reproducibility [15]. Automatic sampling is therefore recommended for NTD.  
125 A syringe pump (New Era Pump System Inc., Farmingdale, NY, USA) was used to pull  
126 headspace samples through the NTD's at a fixed flow rate of 2 mL·min<sup>-1</sup> (Figure 1).

127 For the evaluation of the different sampling methodologies, we used a fixed 5 mL  
128 sample volume in 20 mL crimp-cap HS vials (Supelco). The four sampling  
129 methodologies compared were: (i) conventional static HS sampling (HS), (ii) static HS

130 sampling using the NTD to collect a fixed volume of the headspace (HS-NTD), (iii)  
131 static HS with passive diffusion through the NTD (pHS-NTD), and (iii) active HS  
132 sampling with the NTD (PT-NTD). In (i), 150  $\mu\text{L}$  of headspace air was drawn with a  
133 gas-tight syringe and injected into the GC-MS in splitless mode. In (ii), 4 mL of  
134 headspace air was drawn into the NTD after equilibration. In (iii), the NTD was placed  
135 in the headspace during the thermostated equilibration process allowing the gases  
136 generated to diffuse freely through the NTD (as in a passive sampler). In (iv), the NTD  
137 was placed in the headspace and a purging needle was guided to a nitrogen gas  
138 reservoir. A constant  $\text{N}_2$  purging flow of  $6 \text{ mL}\cdot\text{min}^{-1}$  was maintained during the process.  
139 The headspace was allowed to move through the NTD by the overpressure generated in  
140 the vial.

141 Different approaches as to how to transfer the desorbed sorbents into the GC column  
142 have been discussed by Eom and Pawliszyn [25]. The simplest approach, used in the  
143 present study, is to use the desorptive flow produced by the internal air expansion at the  
144 hot desorption temperatures of the GC injector. No modification of the GC inlet is  
145 required as it is only necessary to fit the appropriate liner [15]. The NTD was inserted  
146 into the injection port in the splitless mode for one minute. After opening the split valve,  
147 the needle was kept in the hot injector for at least 10 minutes. Blank runs were carried  
148 out every five samples but no carry over was observed. Figure 1 in Supplementary  
149 Materials shows the extracted chromatogram of a standard mixture under the desorption  
150 conditions described.

151

### 152 2.3 GC-MS analysis

153 Component separation was achieved by the use of a 30 m long TR-Meta.VOC column  
154 with 0.25 mm I.D. and  $1.5 \mu\text{m}$  film thickness (Teknokroma, Barcelona, Spain). A Focus  
155 GC (Thermo Scientific, Waltham, MA, USA) with a mass spectrometer detector (DSQ  
156 II, Thermo Scientific) was used.

157 The injector (desorption) temperature was maintained at  $300^\circ\text{C}$  to ensure complete and  
158 fast desorption of target VOC's [15,26,27]. The oven temperature program was  $40^\circ\text{C}$  for  
159 2 min, then ramped at  $10^\circ\text{C}\cdot\text{min}^{-1}$  to  $225^\circ\text{C}$  and held for 2 min. Helium carrier gas was  
160 used with a constant inlet flow of  $0.8 \text{ mL}\cdot\text{min}^{-1}$  after purification for water vapor,

161 hydrocarbons and oxygen. MS analyses were carried out in full-scan mode with a scan  
162 range of 40-250 u. Electron impact ionization was applied at 70 eV and the transfer line  
163 was maintained at 230°C. Chromatographic data was acquired by means of Xcalibur  
164 software (v. 1.4, Thermo Electron). Single quantification for each VOC was performed  
165 by analyzing the corresponding extracted ion chromatograms (XIC) at the m/z values  
166 given in bold in Table 1.

167

## 168 2.. Water samples

169 Three urban WWTP's (Castell-Platja d'Aro, Palamós and Blanes), located on the Costa  
170 Brava in north-eastern Spain, were evaluated. The treatment process includes grit  
171 removal and screening, primary settling and activated sludge biological processing in all  
172 plants. The main differences between the plants are in the water reclamation treatment:  
173 at Castell-Platja d'Aro WWTP this consisted of disinfection with UV light and  
174 chlorination, at Palamós it just consisted of chlorination, and at Blanes the treatment  
175 system was not in service during the sampling period.

176 Sampling was performed during April and June 2011. Three samples were taken each  
177 sampling day, collected in independent vials, stored at 4°C, and analyzed within 24  
178 hours. Other water samples evaluated were obtained from a natural stream (La Tordera  
179 stream, sampling downstream from the Blanes WWTP), tap water and commercial  
180 mineral waters.

181

## 182 **3. Results and Discussion**

### 183 3.1. Comparison of sampling methods

184 Conventional static HS was evaluated and compared with the other three sampling  
185 strategies using NTD's. Different working solutions ranging from 20 to 0.002  $\mu\text{g}\cdot\text{L}^{-1}$  for  
186 six target compounds were prepared and measured with the four methodologies. Table 2  
187 shows the lowest concentration detected (LCD's) obtained with the target VOC's. LCD  
188 values correspond to the minimum concentration giving a peak in the chromatogram  
189 with a signal-to-noise ratio  $>5$ .

190 The use of the needle-trap resulted in a significant concentration factor that led to a  
191 reduction in the LCD's (1-2 orders of magnitude between HS and HS-NTD). When the  
192 NTD was placed in the headspace during the thermostated equilibration process (pHS-  
193 NTD), LCD's were still lower than those obtained with conventional static HS, but  
194 higher than those achieved with HS-NTD. Using this sampling methodology, the  
195 passive diffusion occurring during the heating process allowed a portion of the VOC's  
196 to be retained by the NTD. However, as will be seen in the following sections, the time  
197 needed for this sampling methodology to reach maximum efficiency is much longer  
198 than the 50 min used here. The active sampling (PT-NTD) gave the best results for  
199 sensitivity, and LCD's decreased to the units of  $\text{ng}\cdot\text{L}^{-1}$  range.

200 Ridgway et al. [28] evaluated a different needle-trap methodology, known as solid-  
201 phase dynamic extraction (SPDE), and also found that HS-SPDE increased the  
202 sensitivity for BTEX when compared with static HS. However, the use of a PDMS  
203 coating in that study resulted in highly volatile compounds giving a poor response in  
204 HS-SPDE.

205 It is clear that the use of NTD's with appropriate sorbent material gave improved  
206 sensitivity, reaching limits of detection in the range of a few  $\text{ng}\cdot\text{L}^{-1}$ . This presents two  
207 advantages: firstly, it is several orders of magnitude below the regulated values for  
208 VOC's in drinking, natural and waste waters (benzene, due to its carcinogenic risk, has  
209 regulated values of between 1 [29] and 5  $\mu\text{g}\cdot\text{L}^{-1}$  [30] for drinking waters and 50  $\mu\text{g}\cdot\text{L}^{-1}$   
210 for surface waters [22]), and, secondly, the ability to detect VOC's at very low ranges  
211 makes it possible to determine a high percentage of these compounds in water samples  
212 and so provides more accurate information as to their content. Taking into account these  
213 preliminary results, a more detailed evaluation of the adsorption/desorption mechanisms  
214 involved in each sampling procedure was performed before selecting the most  
215 appropriate analytical method.

216

### 217 3.2. Static HS-NTD sampling

218 The main advantage of needle traps is that VOC's are retained by an adsorption  
219 mechanism. By increasing the extraction temperature, the amount of analytes in the  
220 headspace is increased so improving the sensitivity of the method. However, some

221 sensitivity is also lost due to the fact that the increased temperature results in a partial  
222 desorption of the VOC's from the sorbent particles of the NTD. The combined  
223 adsorption/desorption mechanism therefore requires an accurate determination of the  
224 thermostating temperature to find the optimum sampling conditions when working with  
225 NTD's.

226 Previous studies analyzing BTEX using divinylbenzene [9] and Carboxpack X [20] as  
227 sorbents showed that breakthrough for benzene occurred at temperatures above 40°C,  
228 but that increased temperatures resulted in greater sensitivity for the other BTEX. We  
229 compared the results obtained by thermostating at 35°C and 50°C for 60 minutes. It was  
230 found that all 18 VOC's evaluated gave better sensitivity at 50°C. The increase obtained  
231 for the most volatile compounds (dichloromethane and chloroform) was ~60%. The  
232 response increased by 70% in the case of benzene, 90-100% for 1,2-dichloropropane,  
233 toluene and chlorobenzene, and 120-130% for the other less volatile compounds. The  
234 reduced increase observed for the most volatile compounds may be attributed to the  
235 breakthrough described in previous studies [9,20]. Increasing the temperature had the  
236 opposite effect on the repeatability. Precision was better at 35°C (RSD ranging from 3%  
237 for *o*-xylene to 15% for dichloromethane, n=3) than at 50°C (RSD from 8% for  
238 naphthalene to 24% for propylbenzene, n=3). Taking into account that (i) methods with  
239 low detection limits are required for the analysis of VOC's in waters and (ii)  
240 repeatability obtained at 50°C was adequate when working at the ng·L<sup>-1</sup> range, a  
241 compromise thermostating temperature of 50°C was selected for further static HS-NTD  
242 studies.

243 A second parameter evaluated was the equilibration time required to obtain the  
244 maximum sensitivity. It was found that times of around 90 min were required to obtain  
245 the maximum headspace concentration (see Figure 2 in Supplementary Materials),  
246 which is excessive for routine analysis. Moreover, it was found that precision was poor  
247 at larger equilibration times (RSD's ≤15% at 30 min, ≤24% at 60 min and ≤30% at 120  
248 min).

249 Continuous mixing is an effective way to decrease the time needed for equilibration .  
250 Moreover, shaking is recommended for the analysis of nonpolar VOC's when aqueous  
251 solutions exceed 3 mL [23]. The effect of mixing during thermostating was evaluated  
252 and a significant reduction in the equilibration time was observed: <30 min were

253 enough to reach equilibrium under mixing conditions (see Figure 3 in Supplementary  
254 Materials). The use of shorter equilibration times also resulted in better precision (RSD  
255 ranging from 2% for trichlorobenzene to 15% for 1,2-dichloropropane).

256

### 257 3.3. pHS-NTD sampling

258 This sampling methodology is based on the passive diffusion of VOC's through the  
259 sorbent. This process is slow and long equilibration times can be expected. The  
260 evaluation of different sampling times showed a significant increase in the response for  
261 the VOC's evaluated (Figure 2) and equilibrium was not reached after 150 min of  
262 thermostating.

263 It was found that the slow passive diffusion of VOC's along the sorbent trap enhanced  
264 the effect of the temperature in the desorption mechanism described in the previous  
265 section. When sampling at 50°C, competitive desorption of the most volatile compounds  
266 resulted in band broadening along the sorbent bed in the needle trap. This yielded peak  
267 tailing with a shoulder at the back of the peaks for the most volatile compounds (Figure  
268 3). This effect was greater as the volatility of the compound increased and did not allow  
269 quantitative analysis of the most volatile compounds (dichloromethane and chloroform).

270 The desorption process also resulted in increased breakthrough at large sampling times  
271 for highly volatile compounds. As can be seen in Figure 2, compounds with boiling  
272 points >135°C (ethylbenzene, xylenes and 2-ethyltoluene in Figure 2) gave constant  
273 peak area ratio increases, in line with the sampling time ratio increases. The increase in  
274 toluene (b.p. 110.6 °C) was only constant until a sampling time of ~60 min, longer  
275 sampling times resulted in the breakthrough of this compound. In the case of benzene  
276 (b.p. 80.1°C), the presence of a shoulder in the chromatograms confirmed breakthrough  
277 at a sampling time of 30 minutes. Sanchez and Sacks [31] also found that sampling  
278 VOC's from gaseous samples with a microtrap at 40°C resulted in less adsorption of the  
279 most volatile compounds than that achieved at room temperature (25±1°C).

280

### 281 3.4. PT-NTD sampling

282 Dynamic HS, more commonly known as purge-and-trap sampling, can be used to  
283 increase the sensitivity of headspace sampling. Conventional PT instrumentation

284 requires cryogenic devices to help focus the trapped VOC's before they enter the  
285 chromatographic column in order to reduce band broadening. When analyzing aqueous  
286 samples, water content in the headspace is also trapped and may even block the  
287 capillary column by ice formation due to the large amounts of water retained. Thus,  
288 sampling times ~10 min are typically used to reduce the problem with water unless  
289 sophisticated methods for water removal are used [23]. When NTD's have been used to  
290 trap VOC's from aqueous solutions, water has not been found to be a significant  
291 problem [9,18-20].

292 As in the previous sections, we evaluated the effect of sampling time and temperature  
293 by PT-NTD sampling. The use of an N<sub>2</sub> purge at 6 mL·min<sup>-1</sup> helped to reduce the  
294 equilibration time (Figure 4) (45-60 min at 33°C as compared to >150 min with PHS-  
295 NTD) and the limits of detection (see section 3.1).

296 The same desorption mechanism described in previous sections was found with PT-  
297 NTD sampling. Breakthrough took place for those VOC's with boiling times <100°C  
298 after 45-60 min at the two temperatures evaluated (33°C and 50°C) (Figure 4d). Toluene  
299 (b.p. 110°C) only showed breakthrough after 60 min at 50°C and no breakthrough was  
300 observed at 33°C (up to 90 min). Other less volatile compounds did not show  
301 breakthrough at any of the temperatures evaluated.

302 . Repeatability experiments were performed by analyzing three independent sample  
303 vials at 0.6-1.1 µg·L<sup>-1</sup> for each compound. As can be seen in Table 3, RSD's obtained  
304 when purging at 50°C were higher than those at 33°C. Moreover, repeatability values  
305 were independent of the purging time when thermostating at 33°C but were strongly  
306 dependent at 50°C, as can also be observed by the larger error bars obtained at the  
307 longer purging time in Figure 4. These results agree with those obtained by Eom et al.  
308 [9] using sequential purge-and-trap sampling with an NTD. These authors found that no  
309 breakthrough occurs for BTEX at 23°C, but that breakthrough for benzene took place at  
310 temperatures ≥40°C, and for toluene at ≥60°C.

311 Taking into account the mechanism involved with these sampling methodologies, it is  
312 recommended either to sample at low temperatures or cool the needle-trap during the  
313 process for the analysis of highly volatile compounds. The first approach is  
314 instrumentally simpler but has the major limitation that the sampling time required to  
315 reach equilibrium and to obtain limits of detection (LOD) below those achieved with

316 static HS-NTD increases significantly. The second approach requires the development  
317 of more complex instrumentation and was not evaluated in the present study. Static HS-  
318 NTD, however, has shown adequate results for analyzing VOC's in natural and  
319 wastewaters with LOD's below regulated levels using simple and robust  
320 instrumentation.

321

### 322 3.5. Figures of merit of the HS-NTD sampling methodology

323 Static HS-NTD (5 mL sample in 20 mL HS vial,  $\beta=3.0$ ) without stirring (50°C for 60  
324 min) and with mixing (50°C for 30 min) were evaluated. Calibration standard mixtures  
325 (n=8) in the range 0.01 to 50  $\mu\text{g}\cdot\text{L}^{-1}$  for each compound were analyzed applying both  
326 methods. Chloroform and dichloromethane were excluded from the calibrations to avoid  
327 contamination as they are solvents that are commonly used in adjacent laboratories.

328 Table 4 shows the figure of merits obtained in these experiments (see Table 1 in  
329 Supplementary Materials for figures of merit corresponding to PT-NTD). LOD's were  
330 calculated by measuring a standard at 0.1-0.3  $\mu\text{g}\cdot\text{L}^{-1}$  (n=3), taking the SD obtained as  
331 the SD of the blank ( $\text{SD}_{\text{blank}}$ ) and applying the  $3\text{SD}_{\text{blank}}$  criteria. Moreover, positive  
332 detection was confirmed by preparing a standard at the calculated value and measuring  
333 it with the HS-NTD method (n=2). A signal-to-noise ratio  $>3$  was obtained for all the  
334 compounds at the LOD's proposed. Limit of quantification (LOQ) values correspond to  
335 the first standard following a linear trend in the calibration curves and giving a peak  
336  $>10\text{SD}_{\text{blank}}$ . The higher limits obtained without mixing the solutions were mainly due to  
337 the greater RSD's obtained at the longer thermostating times required in this sampling  
338 mode. Linearity was confirmed for both methods in the range of LOQ to 50  $\mu\text{g}\cdot\text{L}^{-1}$  by  
339 evaluating residual distribution. Good fits were achieved for all compounds ( $R^2>0.96$ ).  
340 Mixing the solution during the thermostating was selected for the evaluation of the  
341 water samples as it resulted in reduced sampling time, improved precision and lower  
342 LOD's.

343 Recoveries, repeatability and reproducibility were evaluated with the mixing HS-NTD  
344 method (Table 5). Samples obtained at the effluent of the tertiary treatment from one of  
345 the WWTP's and fortified at the levels indicated in Table 5 were used for these  
346 measurements. Recoveries were obtained after the analysis of a WWTP sample before

347 and after fortification using the same NTD (n=3). Repeatability was determined after  
348 consecutive analyses of three fortified samples. Reproducibility values were obtained  
349 after the analysis of the same fortified sample with five different NTD's. All  
350 compounds gave repeatability and reproducibility values within the precision limits  
351 suggested by the AOAC for single laboratory validation (maximum recommended RSD  
352 of 15% and 32% respectively) [32]. Recoveries obtained were also adequate  
353 (recommended limits 70-125% at 10 ppb range) for all compounds except for  
354 n-butylbenzene, which gave a 50% recovery.

355 The analytical "life" of an NTD was evaluated. It was found that it strongly depends on  
356 the conditioning time used at the hot injector. When the needle trap was maintained in  
357 the injector (300°C) for 20 minutes for cleaning, an average life time of 70 consecutive  
358 analyses were obtained for repeatable figure of merits (n=5). If the conditioning time  
359 was decreased to 10 minutes, the life time of the needle trap was increased to around  
360 100 analyses (n=4). This value represents a limitation when compared with the most  
361 recent SPME fibers, which allow about 200 samples in headspace. A careful evaluation  
362 of the conditioning and maintenance conditions can significantly increase the life of the  
363 needle traps. Sanchez and Sacks evaluated a capillary trap that performed efficiently for  
364 more than 500 consecutive samples [31].

365

### 366 3.6. Analysis of water samples

367 Table 6 shows the minimum and maximum concentrations found in each WWTP at the  
368 different sampling points. Those VOC's that were not detected in any sample (1,2-  
369 dichloropropane, chlorobenzene, 2-chlorotoluene, and 4-chlorotoluene) have been left  
370 out of Table 6.

371 Although these are preliminary analyses to confirm the applicability of the needle-trap  
372 methodology, some trends can be observed from the results obtained. Firstly, all  
373 WWTP's gave similar VOC levels. This agrees with the information obtained from the  
374 plants, which only receive domestic wastewaters, with no industrial inputs, and have  
375 similar equivalent populations for each plant (175,000 habitants for Castell-Platja  
376 d'Aro, 165,450 for Palamós and 109,985 for Blanes). Secondly, the compound present  
377 at the highest levels in all samples was toluene, which was also the VOC present at the

378 highest concentrations in atmospheric air in the surrounding areas of the plants (data not  
379 shown). Thirdly, the levels detected for VOC's at the effluent of the plants represent a  
380 significant reduction of these compounds except for the most volatile compound  
381 (benzene), which showed similar levels at all sampling points within any one WWTP.

382 Other water samples analyzed correspond to a natural stream, tap water and commercial  
383 mineral waters. After evaluating three samples for each type of water, the only  
384 compound found to reach quantifiable levels in all samples was toluene (mean  
385 concentrations were 0.05, 0.04 and 0.12  $\mu\text{g}\cdot\text{L}^{-1}$  for tap, mineral and natural stream  
386 waters respectively). Ethylbenzene was detected in the three types of waters, *p*-xylene  
387 was detected in tap water and the natural stream, and *n*-butylbenzene and naphthalene  
388 were only detected in the natural stream.

389 The results obtained confirm the applicability of the needle-trap methodology and show  
390 that all samples presented levels of VOC's that were below regulated levels and in  
391 accordance with environmental quality standards [22]. In the case of wastewaters,  
392 toluene, the compound found at the highest level (11.13  $\mu\text{g}\cdot\text{L}^{-1}$ ) did not reach the  
393 recommended maximum concentration set by Spanish regulations (50  $\mu\text{g}\cdot\text{L}^{-1}$ ) at the  
394 effluent of the plants. The results obtained are broadly similar to levels detected in  
395 other studies evaluating VOC's in WWTP's [33-37], where only a few industrial plants  
396 occasionally showed higher values, especially for toluene, at influent sampling points  
397 [33,35,37].

398 For surface and drinking waters, the levels of toluene detected agree with those found in  
399 the literature (usually  $<0.5 \mu\text{g}\cdot\text{L}^{-1}$  for drinking waters) and are well below tolerable  
400 daily intakes set for drinking waters by the World Health Organization (70  $\mu\text{g}\cdot\text{L}^{-1}$ ) [38].  
401 The fact that benzene was not detected confirms that this compound is also below  
402 regulated levels [29,30].

403

#### 404 **4. Conclusions**

405 The combination of needle-trap devices and headspace sampling has given improved  
406 method sensitivity, allowing LOD's in the range of  $\text{ng}\cdot\text{L}^{-1}$  to be reached. It should be  
407 noted that these limits are slightly below the LOD's reported with conventional PT  
408 [3,33,34] and the SPME [35] method.

409 The simplicity of the needle-trap technique allows for the fast analysis of VOC's in  
410 aqueous samples. Of the different sampling methodologies compared, static HS-NTD  
411 and PT-NTD were found to give the best results. HS-NTD results in simpler sampling  
412 as it does not require the use of any extra instrumentation. PT-NTD requires a more  
413 exhaustive control of the thermostating process due to the adsorption/desorption  
414 mechanism that takes place simultaneously on the sorbent surface. Using this sampling  
415 methodology, purging at temperatures above 40°C increases the possibility of  
416 breakthrough for those VOC's with boiling points <100°C. However, the larger  
417 concentration factor that can be achieved with PT-NTD leads us to conclude that  
418 detection limits in the range of  $\text{pg}\cdot\text{L}^{-1}$  can be expected once an efficient automatic  
419 sampling procedure has been developed.

420

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429

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- 504

504 **Figure Captions**

505

506 **Figure 1.** Scheme of an NTD (left) and the system used for HS-NTD sampling (right).

507 A: spiral plug; C: Carboxen 1000; T: Tenax TA.

508

509 **Figure 2.** Sampling heating time profiles for VOC analysis by static pHS-NTD  
510 sampling. Experimental conditions: standards at 2-3  $\mu\text{g}\cdot\text{L}^{-1}$  range, thermostating at  
511 50°C. Y-axes values normalized to the peak areas obtained after 30 min thermostating.

512

513 **Figure 3.** Extracted chromatograms (XIC) from a standard analyzed by pHS-NTD. (a)  
514 XIC at  $m/z=78$  (benzene), (b) XIC at  $m/z=91$  (toluene). Experimental conditions:  
515 standard at 2-3  $\mu\text{g}\cdot\text{L}^{-1}$ , thermostating for 60 min at 50°C.

516

517 **Figure 4.** Sampling heating time profiles for VOC analysis by PT-NTD sampling. (a) 2-  
518 ethylbenzene, (b) *o*-xylene, (c) 1,2,3-trichlorobenzene, and (d) 1,2-dichloropropane.  
519 Experimental conditions: standards at 2-3  $\mu\text{g}\cdot\text{L}^{-1}$  range,  $\text{N}_2$  purging at 6  $\text{mL}\cdot\text{min}^{-1}$  at  
520 50°C, 3 replicates at each sampling time.

521

522

523

524 Table 2. Experimental lowest concentrations detected (LOC's) with the four sampling methods  
525 evaluated.

526

Compound	LOC ( $\mu\text{g}\cdot\text{L}^{-1}$ )			
	HS	HS-NTD <sup>a</sup>	pHS-NTD <sup>b</sup>	PT-NTD <sup>c</sup>
benzene	5.0	0.04	1.0	0.002
toluene	0.6	0.01	0.1	0.002

ethylbenzene	0.5	0.01	0.1	0.002
p-xylene	1.5	0.01	0.1	0.002
o-xylene	0.7	0.01	0.1	0.002
2-ethyltoluene	1.0	0.02	0.2	0.002

527 <sup>a</sup> 50 min equilibration at 50°C, then sucking 4 mL headspace through the NTD at 2 mL·min<sup>-1</sup>

528 <sup>b</sup> passive diffusion during 50 min at 50°C

529 <sup>c</sup> 45 min equilibration at 50°C with a N<sub>2</sub> purge at 6 mL·min<sup>-1</sup>

530

## Highlights

1. Headspace sampling with an NTD to determine priority VOC's in water is studied.
2. Needle-trap extraction gives better sensitivity and efficiency compared with HS.
3. LOD's at ng/L are easily achieved by concentration of a HS sample with an NTD.

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Figure 1

Figure 1

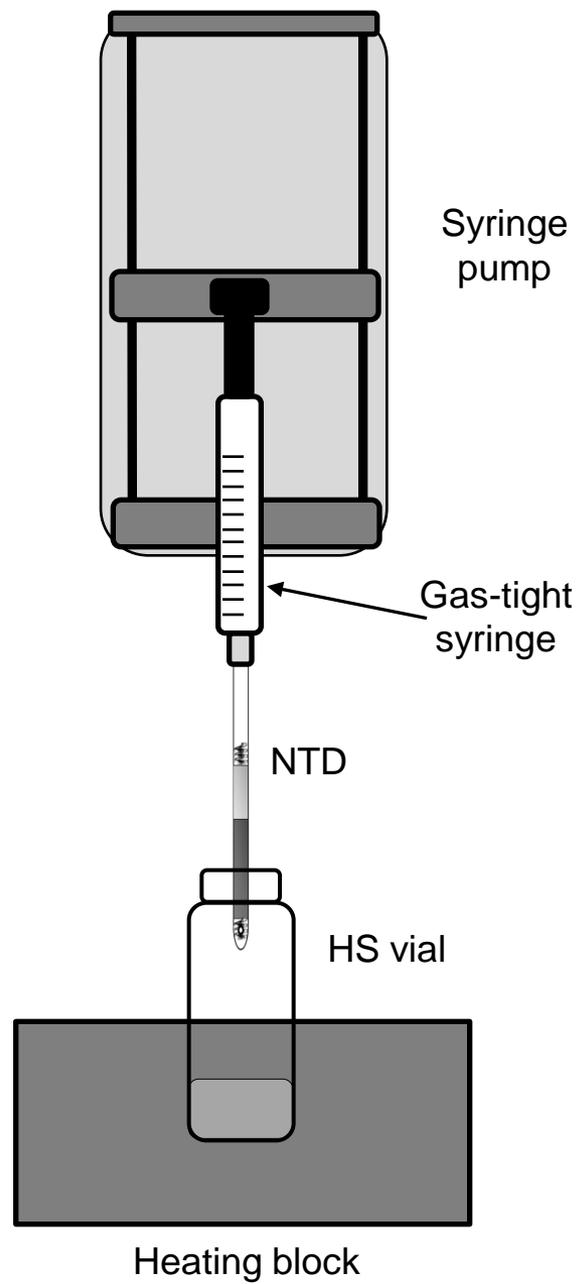
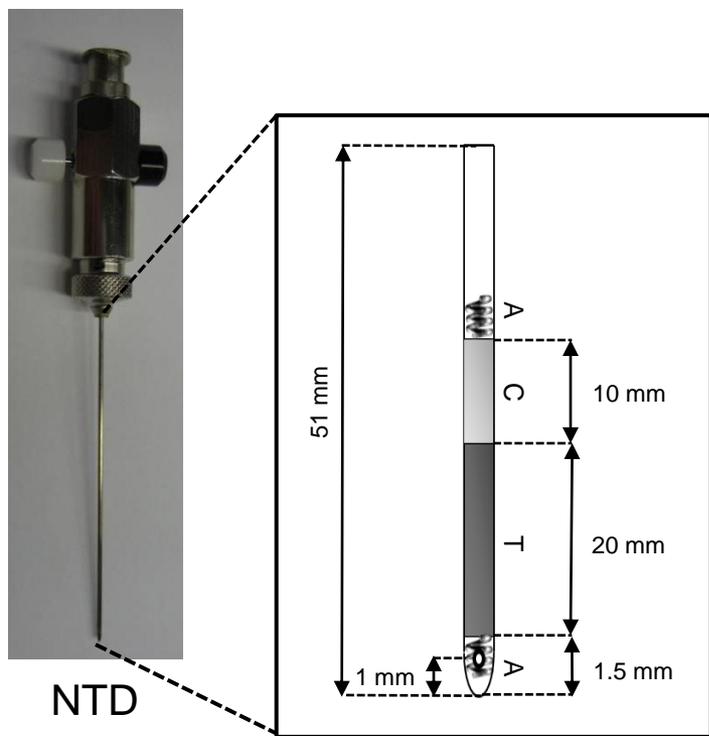
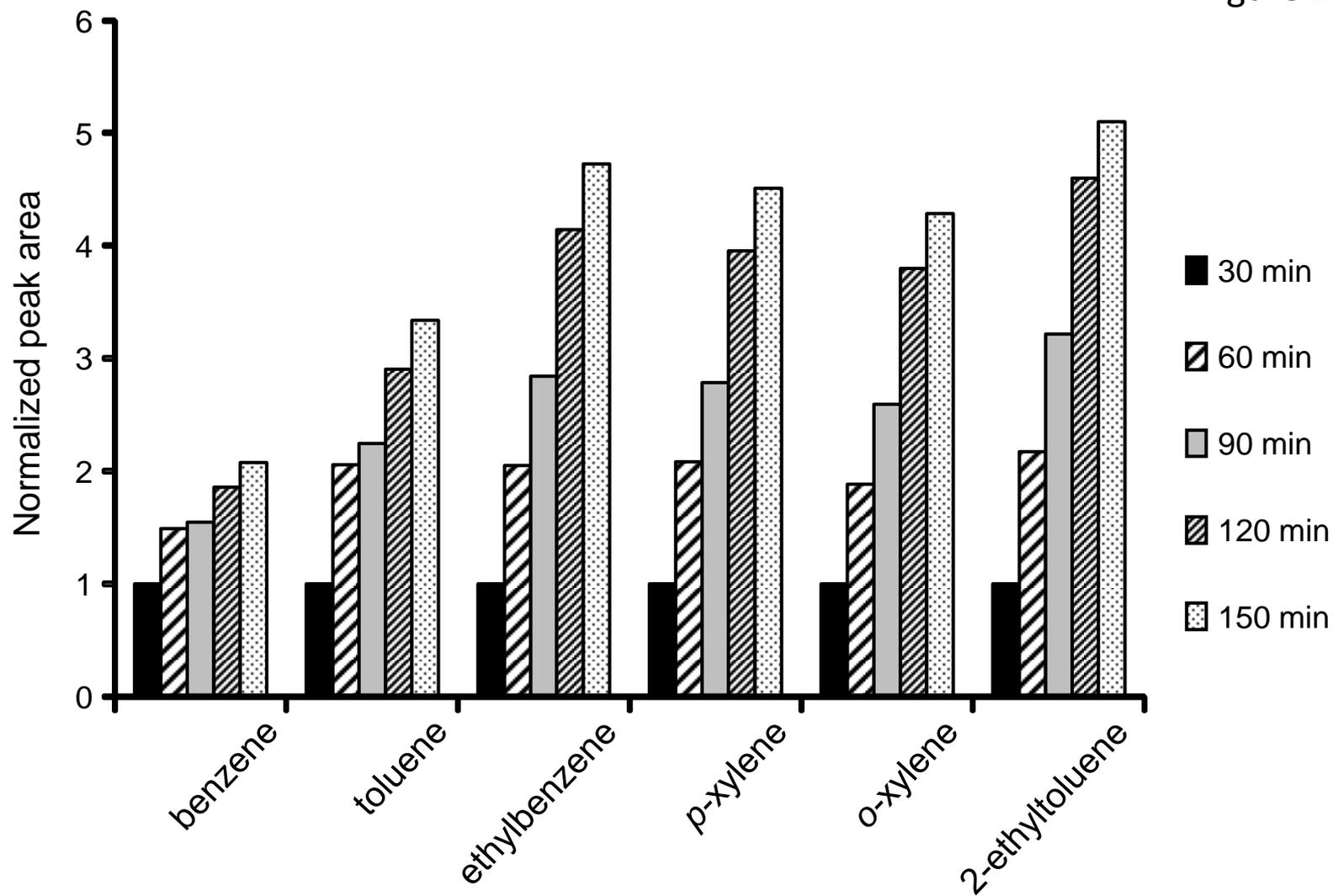


Figure 2

Figure 2



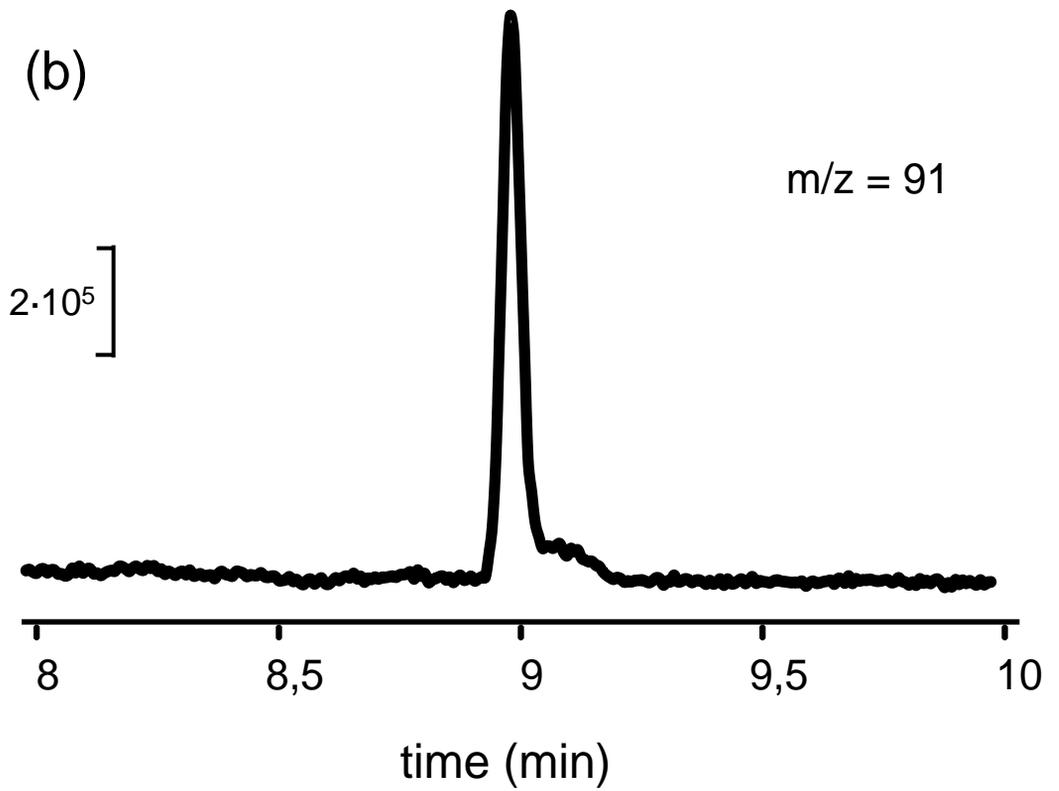
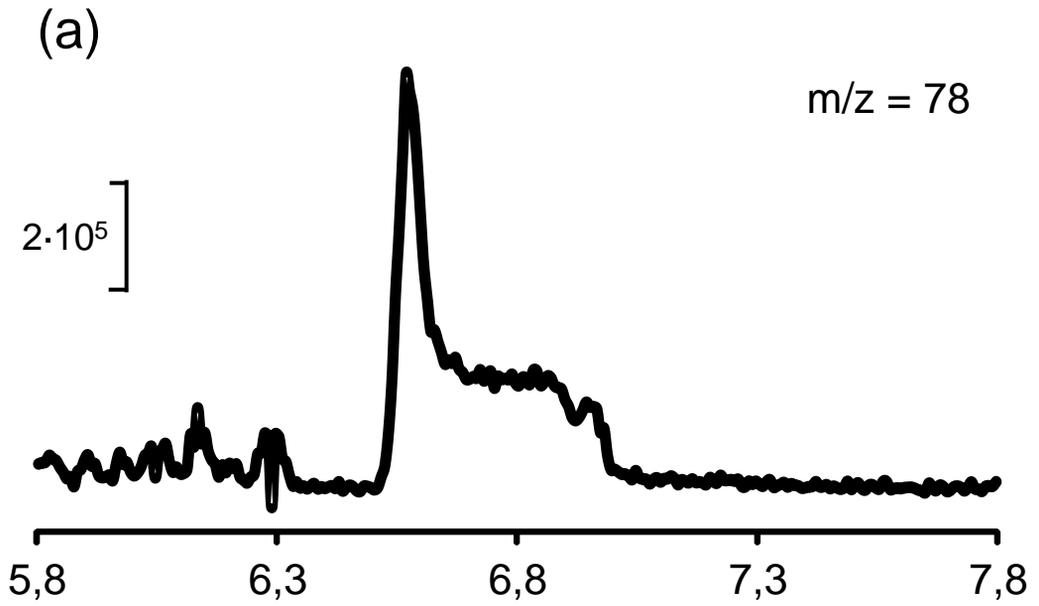
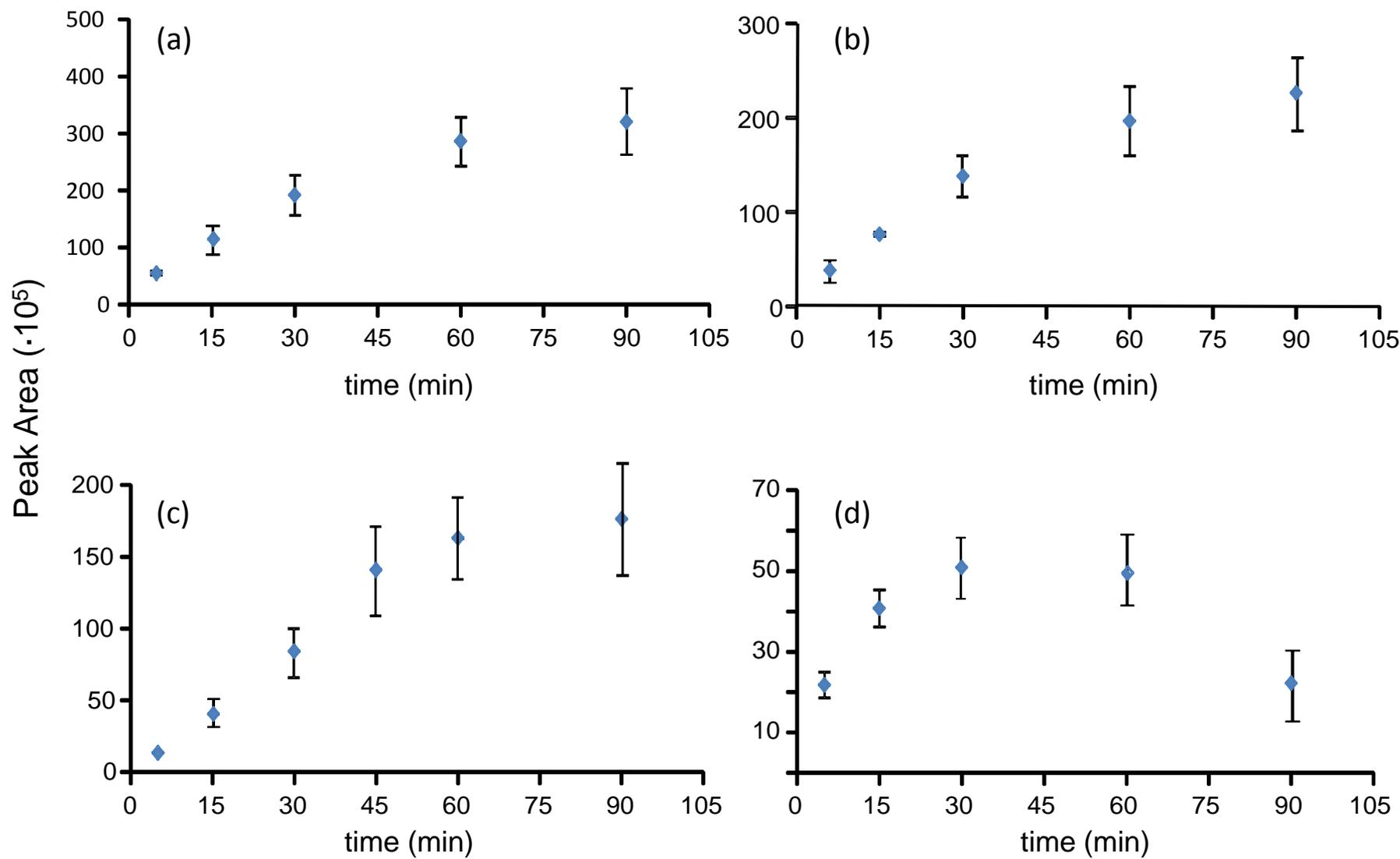


Figure 4

Figure 4



**Table 1.** Volatile compounds evaluated.

	<b>Compound name</b>	<b>Retention time (min)</b>	<b>Characteristic masses<sup>a</sup></b>	<b>b.p. (°C)</b>
1	dichloromethane	3.90	49, <b>84</b> , 86	39.8
2	chloroform	5.58	<b>83</b> , 85	61
3	benzene	6.67	77, <b>78</b>	80.1
4	1,2-dichloropropane	7.52	<b>63</b> , 112	95
5	toluene	8.99	<b>91</b> , 92	110.6
6	chlorobenzene	10.94	77, <b>112</b> , 114	131
7	ethylbenzene	11.01	<b>91</b> , 106	136
8	p-xylene	11.10	91, <b>106</b>	138.3
9	o-xylene	11.75	91, <b>106</b>	144
10	propylbenzene	12.83	<b>91</b> , 120	159
11	2-chlorotoluene	13.11	<b>91</b> , 126	159.2
12	4-chlorotoluene	13.17	<b>91</b> , 126	161.9
13	2-ethyltoluene	13.47	<b>105</b> , 120	165.2
14	n-butylbenzene	14.74	<b>91</b> , 134	183
15	1,2-dichlorobenzene	15.00	111, <b>146</b> , 148	180.5
16	1,2,4-trichlorobenzene	17.53	<b>180</b> , 182	214.4
17	naphthalene	17.98	<b>128</b>	218
18	1,2,3-trichlorobenzene	18.34	<b>180</b> , 182	218.5

<sup>a</sup> primary quantitation ion is given in bold

**Table 3.** Repeatability values (RSD, n=3) obtained with the PT-NTD method at two thermostating temperatures and purging times. N<sub>2</sub> purging at 6 mL·min<sup>-1</sup>.

Compound	Concentration ( $\mu\text{g}\cdot\text{L}^{-1}$ )	Thermostating temperature			
		50°C		33°C	
		Purging time		Purging time	
		15 min	60 min	15 min	60 min
benzene	1.1	23 %	>40 %	14 %	10 %
toluene	0.6	25 %	35 %	14 %	12 %
ethylbenzene	0.7	21 %	17 %	11 %	8 %
<i>p</i> -xylene	0.6	23 %	22 %	8 %	15 %
<i>o</i> -xylene	0.6	19 %	14 %	14 %	14 %
2-ethyltoluene	0.6	17 %	21 %	15 %	14 %

**Table 4.** Linearity parameters, determination coefficients ( $R^2$ ) and limits of detection (LOD) and quantification (LOQ) for the 16 target VOC's with the two proposed sampling methodologies. **LOD and LOQ are in  $\mu\text{g}\cdot\text{L}^{-1}$ .**

Compound	Static HS-NTD (no stirring)				Static HS-NTD (stirring)			
	slope (SD) ( $\cdot 10^6$ )	$R^2$	LOD	LOQ	slope (SD) ( $\cdot 10^6$ )	$R^2$	LOD	LOQ
benzene	4.3 (0.3)	0.991	0.22	0.84	10 (1)	0.981	0.01	0.07
1,2-dichloropropane	2.13 (0.07)	0.985	0.24	1.10	3.6 (0.5)	0.973	0.05	0.09
toluene	6.6 (0.2)	0.975	0.22	0.83	16 (1)	0.987	0.01	0.07
chlorobenzene	4.0 (0.2)	0.967	0.24	1.06	9.0 (0.8)	0.987	0.02	0.09
ethylbenzene	6.9 (0.2)	0.975	0.24	0.83	18 (2)	0.989	0.01	0.07
<i>p</i> -xylene	5.1 (0.1)	0.969	0.25	0.82	13 (1)	0.990	0.01	0.07
<i>o</i> -xylene	6.2 (0.3)	0.986	0.19	0.82	15 (1)	0.990	0.01	0.07
propylbenzene	7.4 (0.2)	0.975	0.23	0.82	23 (3)	0.982	0.01	0.07
2-chlorotoluene	4.8 (0.1)	0.983	0.30	1.03	12 (1)	0.987	0.04	0.09
4-chlorotoluene	4.6 (0.2)	0.969	0.24	1.01	11 (1)	0.986	0.04	0.08
2-ethyltoluene	8.2 (0.4)	0.989	0.19	0.77	19 (2)	0.989	0.03	0.08
n-butylbenzene	5.2 (0.2)	0.969	0.25	0.82	17 (1)	0.990	0.03	0.07
1,2-dichlorobenzene	3.6 (0.1)	0.964	0.18	1.24	6.7 (0.5)	0.991	0.05	0.10
1,2,4-trichlorobenzene	2.04 (0.05)	0.977	0.19	1.39	5.4 (0.3)	0.996	0.06	0.12
naphthalene	4.2 (0.3)	0.984	0.10	0.77	5.9 (0.4)	0.992	0.03	0.07
1,2,3-trichlorobenzene	1.85 (0.05)	0.985	0.16	0.81	3.2 (0.2)	0.992	0.04	0.09

**Table 5.** Recoveries (% , n=3), repeatability (n=3) and reproducibility (n=5) obtained with the HS-NTD sampling method proposed.

<b>Compound</b>	<b>Fortified level</b> <b>(<math>\mu\text{g}\cdot\text{L}^{-1}</math>)</b>	<b>Recovery<sup>a</sup></b> <b>(%)</b>	<b>Repeatability<sup>b</sup></b> <b>(RSD)</b>	<b>Reproducibility<sup>c</sup></b> <b>(RSD)</b>
benzene	6.98	89	9	25
1,2-dichloropropane	9.16	78	7	23
toluene	6.91	87	5	23
chlorobenzene	8.80	75	12	18
ethylbenzene	6.92	68	9	21
<i>p</i> -xylene	6.82	83	13	20
<i>o</i> -xylene	6.83	99	10	19
propylbenzene	6.83	63	11	21
2-chlorotoluene	8.58	70	11	22
4-chlorotoluene	8.39	65	11	16
2-ethyltoluene	6.39	70	4	25
n-butylbenzene	6.81	50	8	22
1,2-dichlorobenzene	10.34	71	7	18
1,2,4-trichlorobenzene	11.56	65	4	18
naphthalene	6.47	93	3	18
1,2,3-trichlorobenzene	6.38	98	2	15

<sup>a</sup> Mean of three consecutive analysis with the same needle-trap.

<sup>b</sup> Relative standard deviations determined after three consecutive analysis of the fortified sample with the same needle-trap.

<sup>c</sup> Relative standard deviations obtained in the analysis of the same fortified sample with five different needle-traps.

**Table 6.** Minimum and maximum concentrations found for the target VOC's ( $\mu\text{g}\cdot\text{L}^{-1}$ ) at different sites of the WWTP's evaluated. Eighteen samples analyzed for Castell-Platja d'Aro WWTP and three samples for Palamós and Blanes WWTP's. Those target VOC's that were not detected in any sample have not been added to the Table.

Compound	WWTP	Sampling point			
		Primary Effluent	Secondary Effluent	Tertiary Effluent	Chlorination
benzene	Castell-Platja d'Aro	0.03-2.16	0.03-2.14	0.03-2.25	d-0.03
	Palamós	0.21-0.24	0.37-0.52	0.21-0.53	NA
	Blanes	d-0.03	d-1.32	NA	NA
toluene	Castell-Platja d'Aro	2.85-20.01	3.10-32.12	0.72-7.90	0.56-4.19
	Palamós	17.72-38.23	6.26-20.91	d-0.07	NA
	Blanes	25.43-47.23	0.57-11.13	NA	NA
ethylbenzene	Castell-Platja d'Aro	d-2.61	0.07-2.56	0.08-2.58	0.08-0.11
	Palamós	d-0.50	nd-d	d-0.17	NA
	Blanes	0.32-0.53	0.12-0.32	NA	NA
<i>p</i> -xylene	Castell-Platja d'Aro	0.06-4.31	0.10-4.16	0.13-4.12	d-0.19
	Palamós	0.97-2.36	nd-d	d-1.22	NA
	Blanes	0.91-1.61	0.31-4.26	NA	NA
<i>o</i> -xylene	Castell-Platja d'Aro	0.31-3.17	0.15-3.10	d-3.09	nd-0.25
	Palamós	0.25-0.65	nd-d	d-0.31	NA
	Blanes	0.26-0.44	0.19-2.00	NA	NA
propylbenzene	Castell-Platja d'Aro	0.04-2.54	0.31-2.52	0.33-2.52	nd-d
	Palamós	nd-d	nd-d	nd-d	NA
	Blanes	0.32-0.37	d-0.27	NA	NA
2-ethyltoluene	Castell-Platja d'Aro	0.34-2.07	0.16-2.04	0.06-2.04	nd-0.17
	Palamós	0.21-1.51	nd-0.03	0.10-0.29	NA
	Blanes	0.30-0.48	0.15-0.20	NA	NA
n-butylbenzene	Castell-Platja d'Aro	d-3.03	d-3.04	0.31-3.03	nd-0.05
	Palamós	nd-d	nd-d	nd-d	NA

	Blanes	0.25-0.29	0.19-0.20	NA	NA
1,2-dichlorobenzene	Castell-Platja d'Aro	0.25-1.11	d-0.77	nd-0.76	nd-d
	Palamós	nd-0.05	nd	nd	NA
	Blanes	0.05-0.40	0.31-0.38	NA	NA
1,2,4-trichlorobenzene	Castell-Platja d'Aro	nd-0.06	nd-d	nd-d	nd-d
	Palamós	nd	nd	nd	NA
	Blanes	nd	nd	NA	NA
naphtalene	Castell-Platja d'Aro	0.44-1.53	d-1.51	d-1.51	nd-d
	Palamós	nd-d	nd-d	nd-d	NA
	Blanes	0.05-0.11	d-0.07	NA	NA
1,2,3-trichlorobenzene	Castell-Platja d'Aro	nd-0.41	nd-0.40	nd-0.41	nd
	Palamós	nd	nd	nd	NA
	Blanes	nd	nd	NA	NA

d – detected but below LOQ

nd – below LCD

NA – not analyzed