Development of needle trap technology for on-site determinations: active and passive sampling

Saba Asl-Hariri[a,**], *German A. Gómez-Ríos*[a,**], *Emanuela Gionfriddo*[a,b], *PeterDawes*[c,d], *JanuszPawliszyn*[a,*]

[a]Department of Chemistry, University of Waterloo, Ontario, Canada N2L 3G1. janusz@uwaterloo.ca (J. Pawliszyn),Tel.: +1 519 888 4641; fax: +1 519 746 0435.

[b]Department of Chemistry and Chemical Technologies, University of Calabria, Arcavacata di Rende (CS), Italy 87036

[c]SGE Analytical Science Pty Ltd, 7 Argent Place, Ringwood, Vic 3134 Australia

Supplementary Information

Section 1.1 Chemicals and Materials

HPLC grade methanol was obtained from Caledon laboratories LTD (Georgetown, ON, Canada). Benzene, toluene, xylene, limonene, α-pinene, β-pinene, and decane were purchased from Sigma-Aldrich (Mississauga, ON, Canada). Helium of ultra-high purity was supplied by Praxair (Kitchener, ON, Canada). Gas tight syringes (1 and 5 mL) were purchased from Hamilton Company (Reno, NE, USA). All the preparations were carried out in a ventilated fume hood. Car particles (surface area: 1200 m2/g) of 60/80 mesh were purchased from Sigma-Aldrich (Bellefonte, PA, USA). DVB particles (surface area: 582 m2/g) of 60/80 mesh were purchased from Ohio Valley (Marietta, OH, USA). The 3.5 inch long 22-gauge blunt needles (I.D. 0.41 mm, O.D. 0.71 mm) were purchased from Dynamedical Corporation (London, ON, Canada). Stainless steel wires (O.D. 100 μm) were purchased from Small Parts (Lexington, KY, US). Extended tip needle traps were provided by SGE Analytical Science (Victoria, Australia).The 5-min epoxy glue was purchased from Henkel Canada (Mississauga, Ontario, Canada). The ADM 1000 flow-meter was purchased from Agilent Technologies (Mississauga, ON, Canada)

Section 1.2 Instrumentation

Indoor air analysis and in situ plant sampling

An Agilent 6890 gas chromatograph coupled to a 5973 MSD quadrupole mass spectrometer (Agilent Technologies, Mississauga, ON, Canada) was used in this study. For the analysis of biogenic emissions, the chromatographic separations were performed using a SLBTM-5MB (30 m x 0.25 mm x 0.25 μm) fused silica column from Sigma–Aldrich, with helium as the carrier gas at a flow rate of 1.5

mL min−1. The oven temperature was initially held at 50 ºC, gradually increased to 60 ºC at a rate of 1 ºC min−1, then increased to 280 ºC at a rate of 30 ºC min−1, finally held for 0.67 min. The chromatographic separations for indoor air analysis were performed using a Rxi®-624Sil MS (30 m x 0.32 mm x 1.80 µm) column from Restek with helium as the carrier gas at a flow rate of 1.5 mL min^{-1}. The oven temperature was initially held at 40 ºC for 2 min, gradually increased to 55 ºC at a rate of 3 ºC min^{-1}, then increased to 250 ºC at a rate of 20 ºC min−1,and finally held for 3.25 min. During the analysis, the transfer line, MS Quad and MS source were set at 280 ºC, 150 ºC and 230 ºC, respectively, with the MS operated in electron ionization mode. Full scan mode (40–250 m/z) was used for all compounds, and quantitation was done using extracted ion chromatograms. The ion m/z 93 was used for quantitative analysis of α-pinene, β-pinene and limonene, while the ion m/z 91 was used for quantitative analysis of toluene. Chromatographic peak identification was made by library matching using the 2002 NIST MS Library (V.2.0 NIST MS Search software).

PDS-NT initial evaluation

An Acme 6100 series gas chromatograph (Young Lin Instruments, Anyang, South Korea) equipped with a flame ionization detector (FID), and a capillary column (RTX-5, 30 m × 0.25 mm I.D., and 0.25µm film thickness) was used for the separation and detection of BTX. The oven temperature was initially held at 40 ºC for 1 min, gradually increased to 180 ºC at a rate of 25 ºC per min, and then held for 2 min. An ATAS GL Optic 3 injection port (ATAS GL, Eindhoven, Netherlands) was used for liquid, needle trap and SPME injections.

Section 1.3 Gas standard solution

Standard Gas Mixture and permeation tubes

Permeation tubes for the analytes under study were made by encapsulating pure analyte inside a 100 mm long (1/4 in.) Teflon™ tubing capped with 20 mm long solid Teflon™ plugs and (1/4) in Swagelok caps. Emission rates for each permeation tube were verified by periodic monitoring of weight loss of individual analyte tubes. A standard gas generator (model 491 MB, Kin-Tech Laboratories, La Marque, TX, USA) was used to generate standard gases with desired concentrations. The permeation tubes made in our laboratory were placed inside a glass chamber, held in a temperature-controlled oven and swept with a controllable constant flow of compressed air. Different concentrations of the analytes were obtained by adjusting both the permeation chamber temperature and the airflow rate.

Sampling chambers. For the analysis of VOCs and semi-VOCs, a sampling chamber, designed by Koziel et al. [1], was installed downstream from the standard gas generators. A schematic of the sampling chamber is provided in **Figure SI-2**[1]. This sampling chamber facilitated a steady-state mass flow of all the standards. The sampling chamber consisted of a custom made 1.5 L glass bulb with several sampling ports that were plugged with Thermogreen LB-2 predrilled septa. Omega 120 W heating tape was wrapped around the glass bulb to control the temperature inside the bulb. An Omega K-type thermocouple was attached to the outside surface of the glass bulb in order to control its internal temperature. Both heating tape and thermocouple were connected to an electronic heat control device constructed by the Electronic Science Shop at the University of Waterloo (UW). Air temperatures in the vicinity of the SPME fibers were maintained within ±1.2% of the adjusted temperature. Standard gas flow rates ranged from 50 to 3000 mL/min, resulting in mean air velocities similar to those

encountered in indoor air environments. Standard gas generators and sampling chambers were validated using a multi-bed needle trap.

For the evaluation of the new pen-like device with BTX, a new sampling chamber was built at the glass blowing shop of the University of Waterloo. A schematic of the sampling chamber is provided in **Figure SI-3**. It was comprised of four sampling ports specially designed to evaluate the pen-device and four additional ports for conventional NT/SPME sampling. This sampling port had a clever system that circumvented the release of contaminants in the laboratory atmosphere. It consisted of two Teflon O-rings embedded within a predrilled Teflon stopper that pressed the pen-device and sealed the system. When the pen was not sampling, a Teflon plug of the same outside diameter was used to seal the system. Custom-made glass restrictions, as well as a special Thermogreen washer were built to hold the Teflon stopper in position by tightening its cap. In order to evaluate multiple devices, four ports symmetrically distributed were constructed following the same design. Standard gas generators and sampling chambers were validated using a multi-bed needle trap. It should be highlighted that during the entire time window in which the experiments were performed, no statistical variation of the probes' concentration in the sampling chamber was noticed. As well, instrumental quality control (QC) tests showed an inter-day variation smaller than 3.5%.

For the extraction of BVOCs emitted by live pine trees, a glass chamber designed by Zini et al. was used [2]. It consisted of a Pyrex glass cylinder (120 mm wide, Ø = 60 mm), where pine needles from a pine tree could be inserted through a hole in one of its ends, as shown in **Figure SI-4**. After the introduction of the small branch, this hole could be sealed using Teflon tape. A round glass lid secured by clamps closed the other end of the chamber. This lid had several 5-mm holes sealed by

Thermogreen LB-2 predrilled septa (Supelco), into which a NT could be introduced to sample the air inside. All glass parts of the container were silanized prior to their use. In order to prevent the presence of artifacts and contamination from previous analyses, the container was cleaned with methanol and dried with a constant nitrogen flow in a fume hood between samplings.

Section 1.4 Sampling Procedures

Sampling and desorption of needle traps

For indoor air sampling and verification of concentrations in the exposure chamber, the NTD was connected to the sampling pump while a volume of the gaseous sample was pumped from the gas standard generator through the needle, at a flow rate of 5 mL/min. After sampling, the NTD was wrapped with aluminum foil and stored in a plastic bag on dry ice. Before injection, the NTD was removed from dry ice and left to reach room temperature. Next, the cap of the tip was removed and then introduced into a GC injector for desorption. Sampling with the NTDs was conducted using a bi-directional syringe pump purchased from Kloehn (Las Vegas, NE, USA). In the case of indoors time-weighted average sampling, needles were placed inside of a personal diffusive sampler and samplings were performed over a period of 8 hours, between 10 am and 6 pm.

On-site and in situ sampling of pine trees

A pine tree branch was sealed in the glass sampling chamber (supporting information, section 1.3), and air inside the chamber was extracted for 1 min using a NT packed with DVB. This procedure was performed every 3 hours between 8 am and 8 pm. Blank analyses of the NTs and glass chamber were run before the start of each sampling. After sampling, NTs were sealed with Teflon caps and kept under dry ice while transported to the laboratory[3]. Time elapsed between sampling and analysis never

exceeded two hours; under these conditions the loss of extracted analytes is expected to be insignificant, as proven by Chen *et al* [3].

Section 2.1 Initial assessment of Needle Traps

As previously described [4,5], the outer diameter of the tube is approximately 500 μm, and it fits tightly inside the restriction of the narrow neck liner (experimental section) providing a dual seal system [5,6]. The inner diameter of the tube is 200 μm, enough to retain sorbent particles, and 1 cm in length. The first prototype evaluated (5 NTs in total) was packed with 2 cm of DVB particles (60/80 mesh) and a small tubing (480 μm) of lesser inner diameter inserted at the back of the packing to hold the particles in place. Numerous parameters were considered in order to have a comprehensive assessment in our study, including a) physical inspection of the NTs before and after usage; b) reproducibility of intra- and inter-NT flow rates reproducibility; c) determination of residual manufacturing of contaminants or sorbent deterioration after multiple uses (chromatographic blank of the NTs), and d) comparison of the amount of analyte collected when performing extractions at different flow rates.

One of the main drawbacks of the initial prototype was the easiness of blocking during sampling and desorption, which was perceived as a diminishing or complete depletion of instrumental signal corresponding to a known concentration. This observation was verified by measuring the NT flow resistance (please refer to experimental section) before and after injection. A careful inspection under the microscope, as seen in **Figure SI-5,** revealed key aspects of blocking: septum pieces from the GC injector or sampling chamber accumulated in the extended tip, as well as small Teflon fragments, coming from the slider, agglomerated at the side hole. In order to verify the cause of NT blocking, a side-hole of the same size was made on a commercial needle, and the surface surrounding the NT side-hole was not smoothed with sand paper. Hereafter, a Teflon slider was passed several times over the

side-hole, simulating the sealing process, and a significant accumulation of Teflon was observed in **Figure SI-6**. Therefore, smoothing and blunting of the side-hole and extended tip, respectively,were suggested to the manufacturer in order to improve the reusability of the NTs. In addition to blocking issues, the needle body showed poor robustness to mechanical stress during the injection step. Thus, some of the needles may bend/break during the desorption step, a critical issue if autosamplers are to be used to increase the throughput of the analysis.

List of Figures

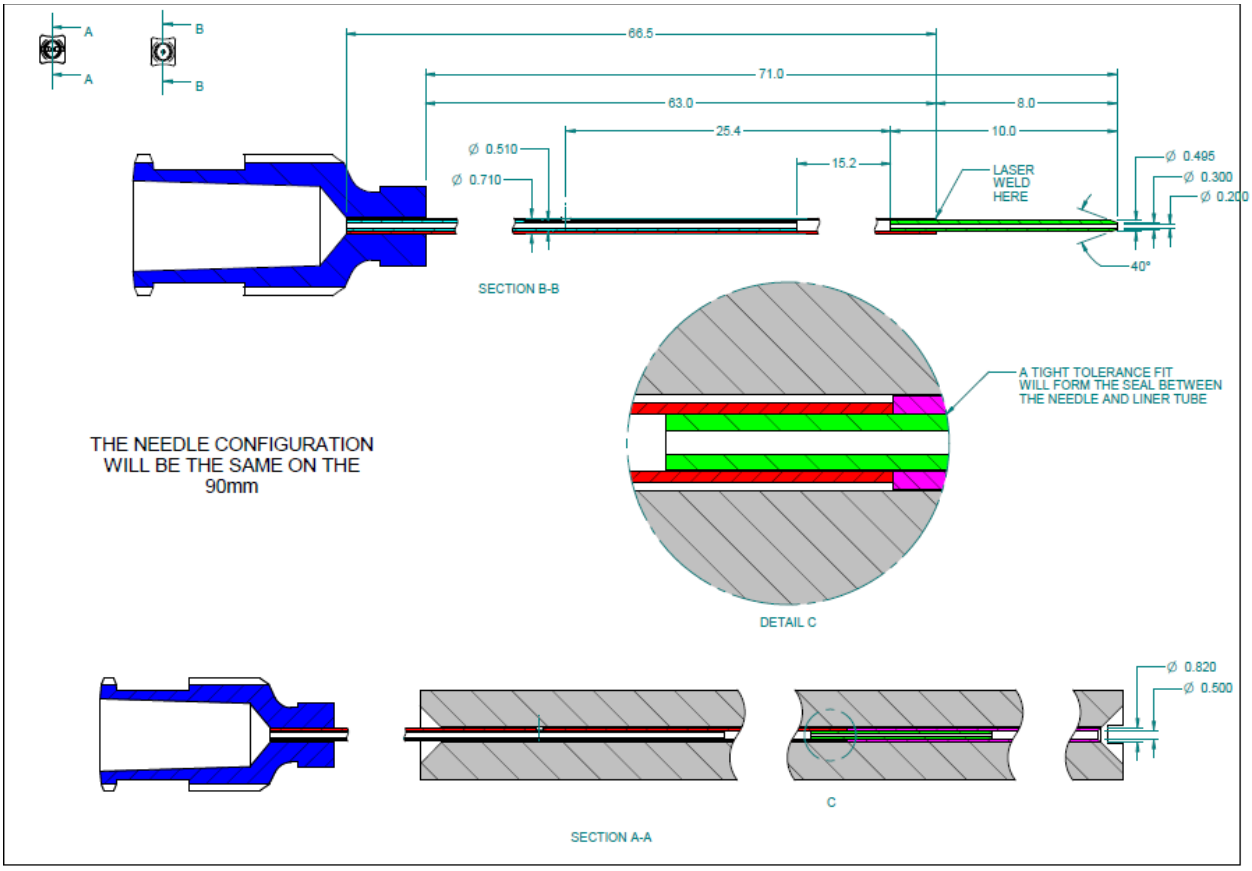


Figure SI-1 Needle trap configuration which designed by SGE Analytical Science

Figure SI-2

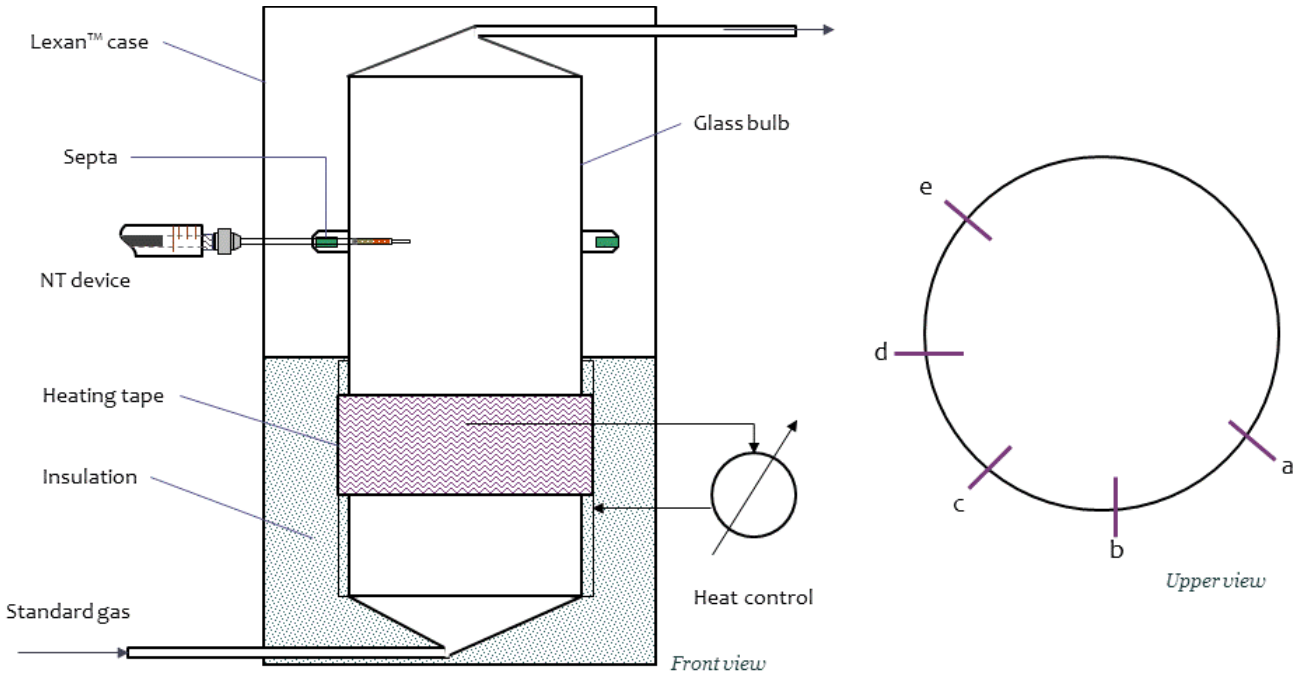


Figure SI-2 Schematic of the sampling chamber for NT extractions [19]

Figure SI-3

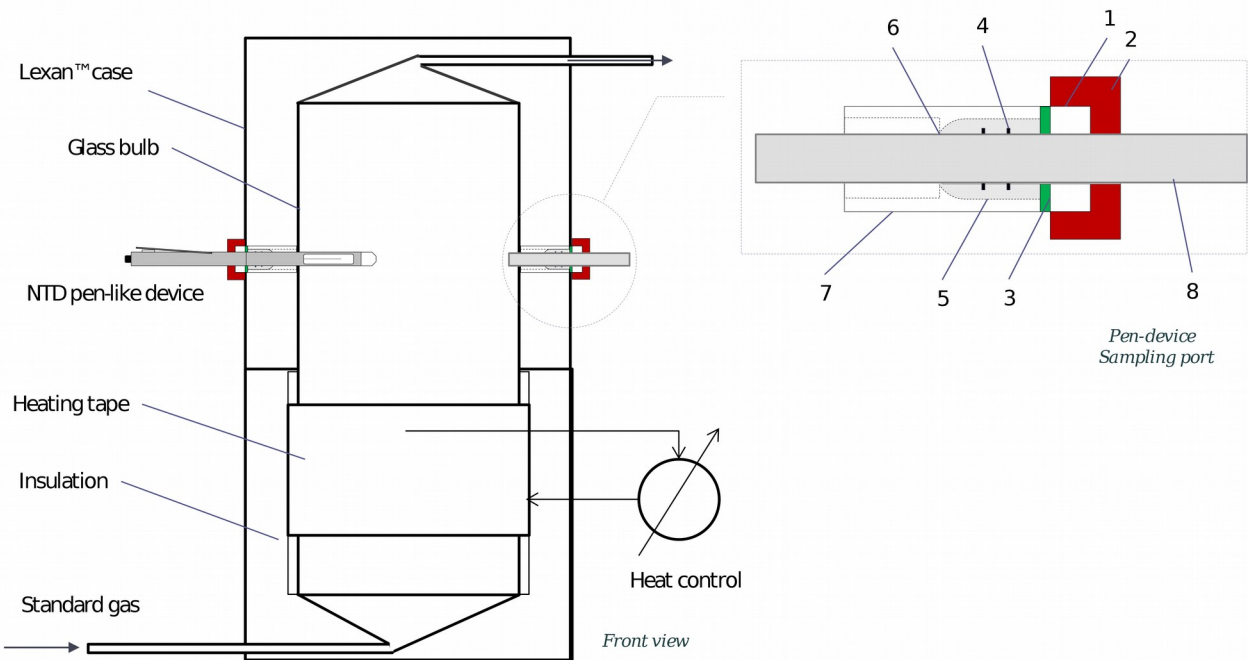


Figure SI-3 Schematic of the sampling chamber used for the evaluation of the pen-like NT diffusive sampler. 1, GL thread; 2, chamber cap; 3, Thermogreen washer; 4, Teflon O-ring; 5, Pre-drilled Teflon stopper; 6, glass restriction; 7, glass tubing; 8, Teflon plug that seals the chamber when the pen is not sampling.

Figure SI-4

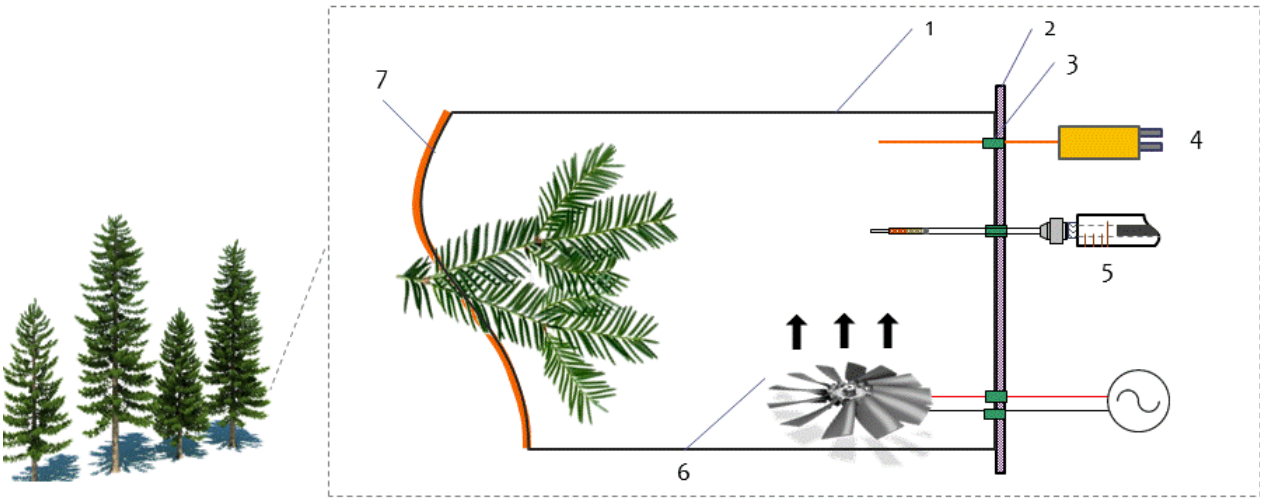


Figure SI-4 Glass container for live plants BVOC extraction: 1, silanized glass cylindrical body (120 mm x 60 mm); 2, silanized glass lid; 3, sampling holes topped with Thermogreen LB-2 septa; 4, thermocouple; 5, NT packed with 2cm DVB; 6, microfan (40 mm x 40 mm x 6 mm); and 7, Teflon tape seal.

Figure SI-5

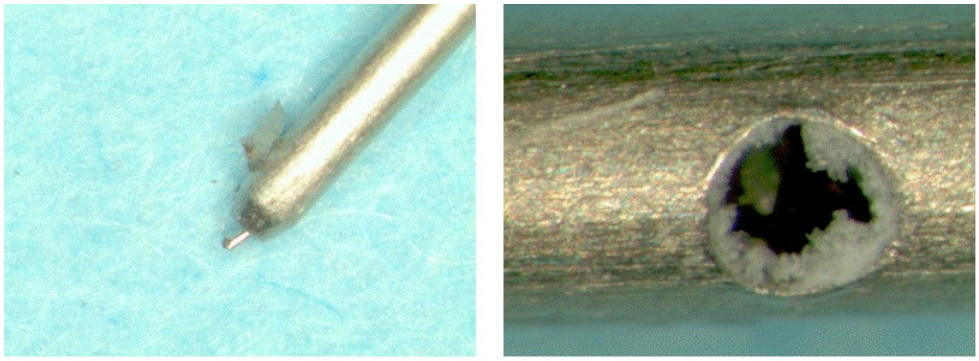


Figure SI-5 Septum and Teflon accumulation after multiple injections

Figure SI-6

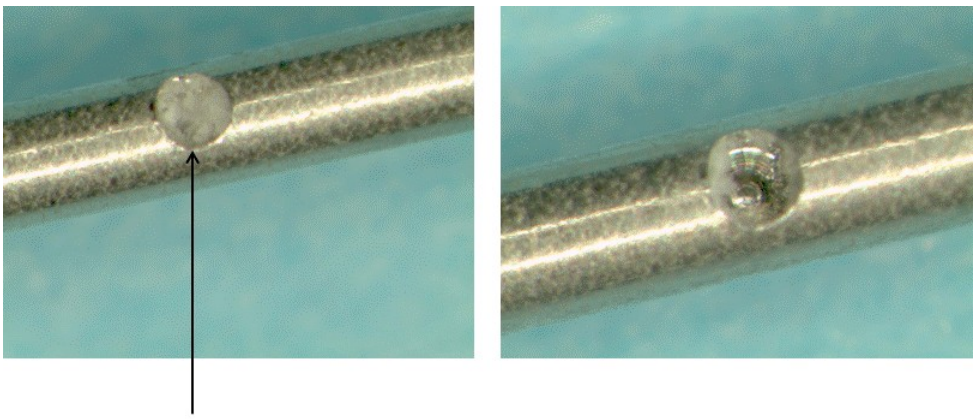


Figure SI-6 Teflon accumulation in a no-polish in-house drilled NT

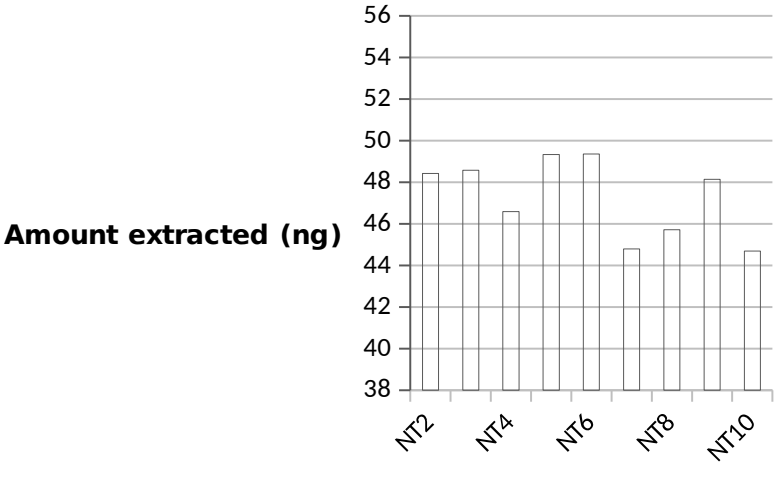
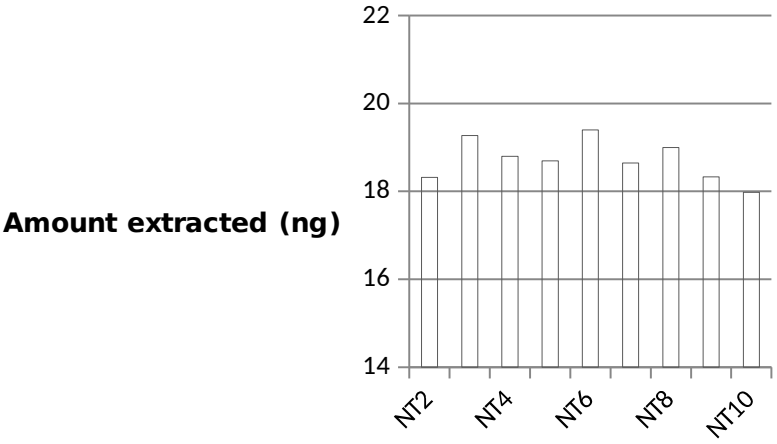

Amount extracted (ng)
56
54
52
50
48
46
44
42
40
38
NT2
NT4
NT6
NT8
NT10

Figure SI-7


Amount extracted (ng)
22
20
18
16
14
NT2
NT4
NT6
NT8
NT10

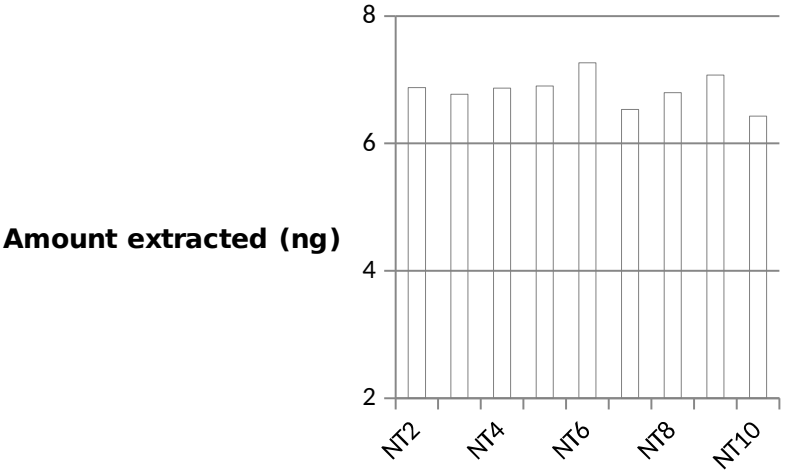


Figure SI-7 (A-C) Comparison of the amount of xylene, decane and limonene extracted by 9 commercial NTs packed with DVB particles. Sample volume was 20 mL at a sampling rate of 5 mL/min.

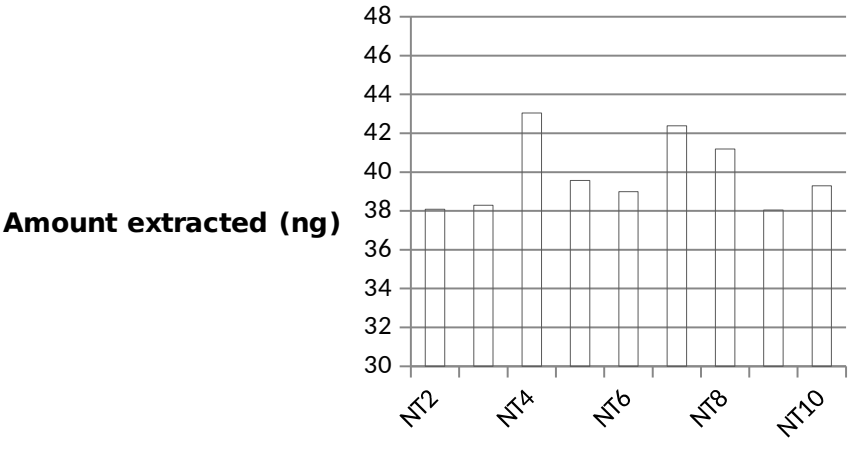


Figure SI-8

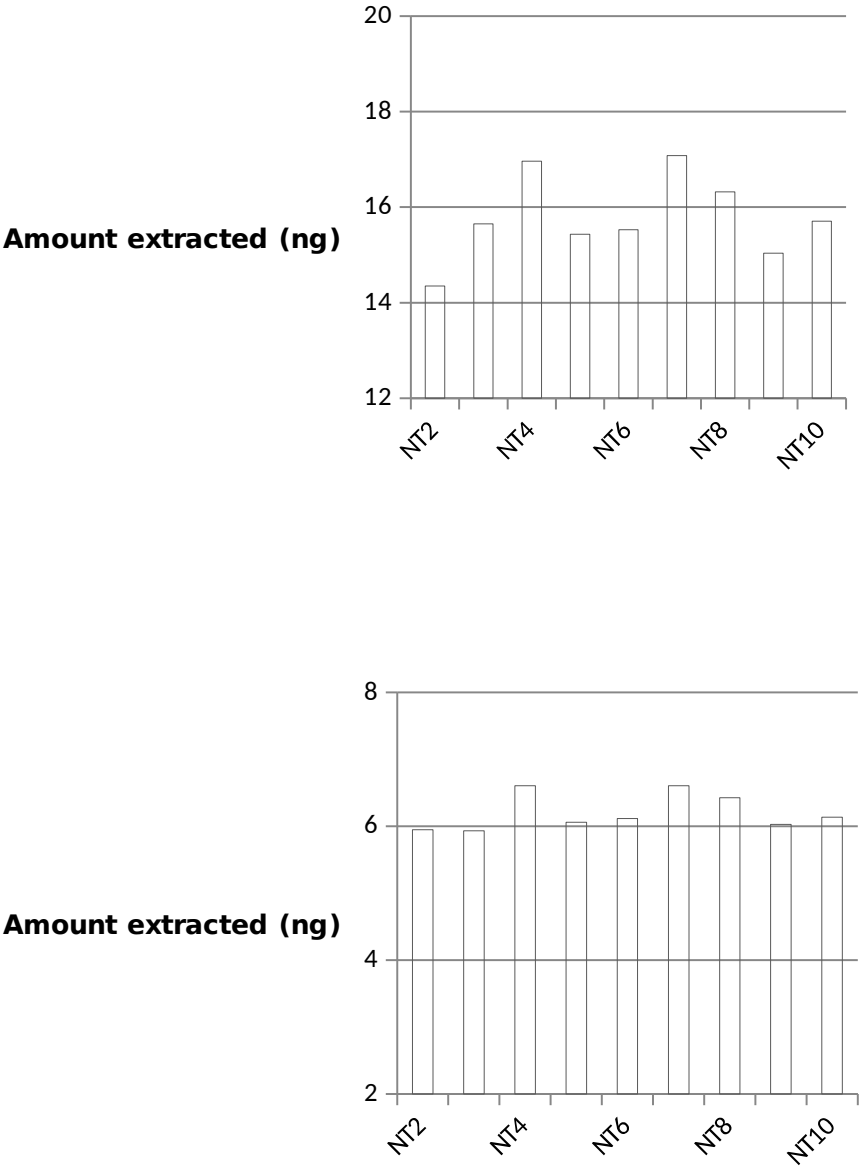


Figure SI-8(A-C) Comparison of the amount of xylene, decane and limonene extracted by 9 commercial NTs packed with DVB particles. Sample volume was 20 mL at a sampling rate of 10 mL/min.

Figure SI-9

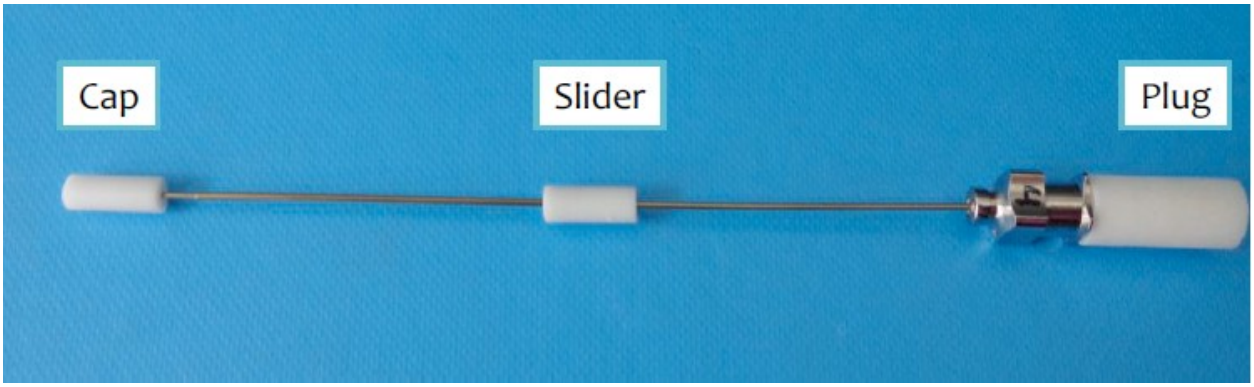


Figure SI-9 Description of a SGE needle trap properly sealed and capped (add here description of the slider)

Figure SI-10

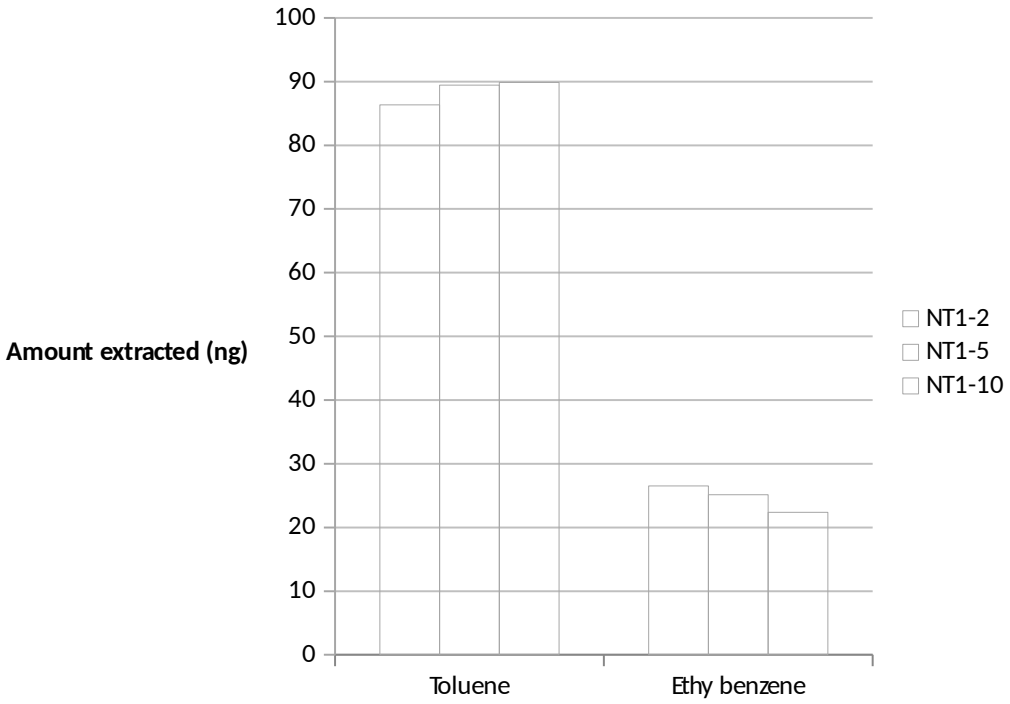


Figure SI-10 Comparison of the amount of extracted by NT1 at different flow rates. Experiments were performed the same day (n=3) at 2, 5 and 10 mL/min.

Figure SI-11

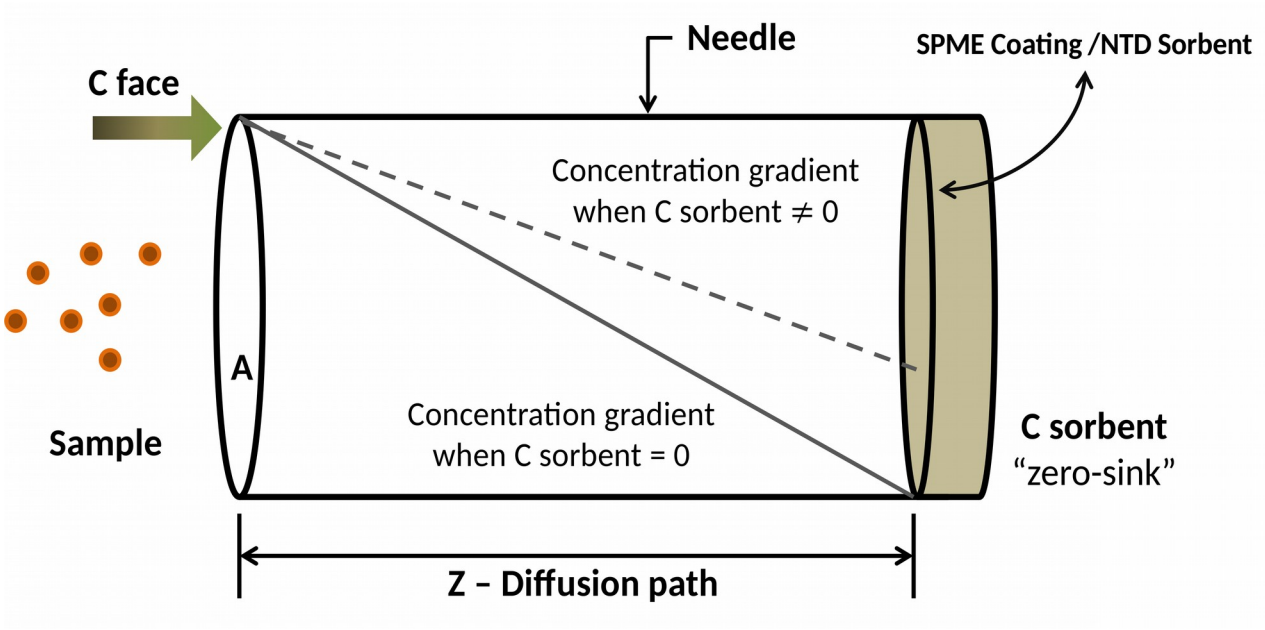


Figure SI-11 Concentration gradient of an analyte produced between the opening of the needle and position of the sorbent Z. Z: diffusion path; $C_{sorbent}$: Concentration near the sorbent interface; C_{face}: time dependent concentration of the analyte at the needle opening; A: area of the cross-section of the diffusion barrier.

Figure SI-12

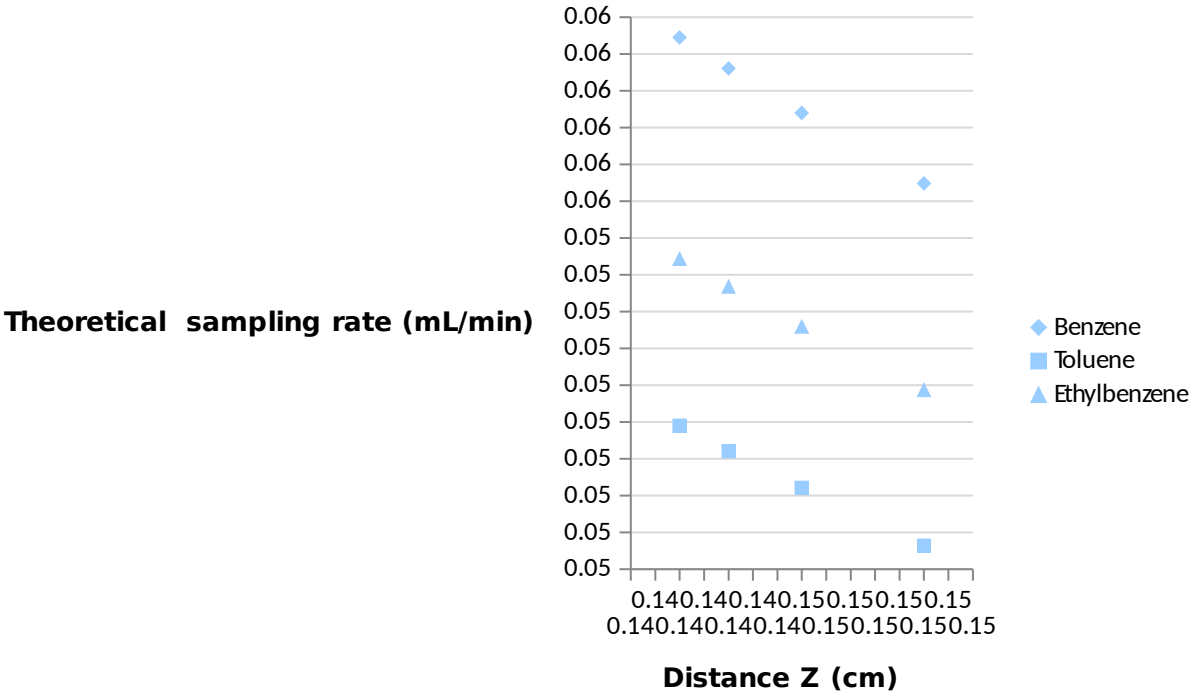


Figure SI-12 Theoretical determination of sampling rates for three probes assuming a temperature of 35 ºC, pressure of 1atm, M_{air} of 28.97 g/mol and $V_{air}$of 20.1 cm^3/mol. Diffusion coefficients were calculated according to the method proposed by Fuller, Schettler, and Giddings (FSG) [27]listed on Equation 2. Sampling rates were calculated according to the equation presented on Table SI-3.

Figure SI-13

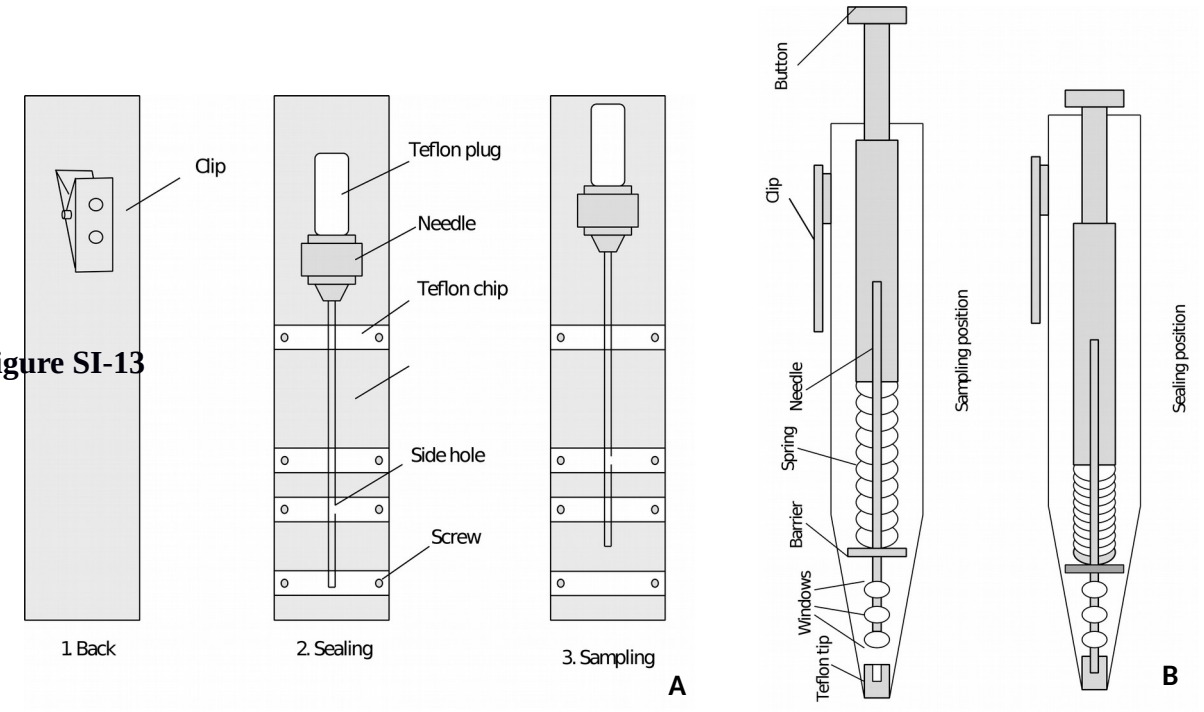


Figure SI-13 Schematic drawing of field samplers developed for NTD in passive mode. A, badge like sampler; B, pen-like sampler. *Images were taken with permission from reference* [5].

Figure SI-14

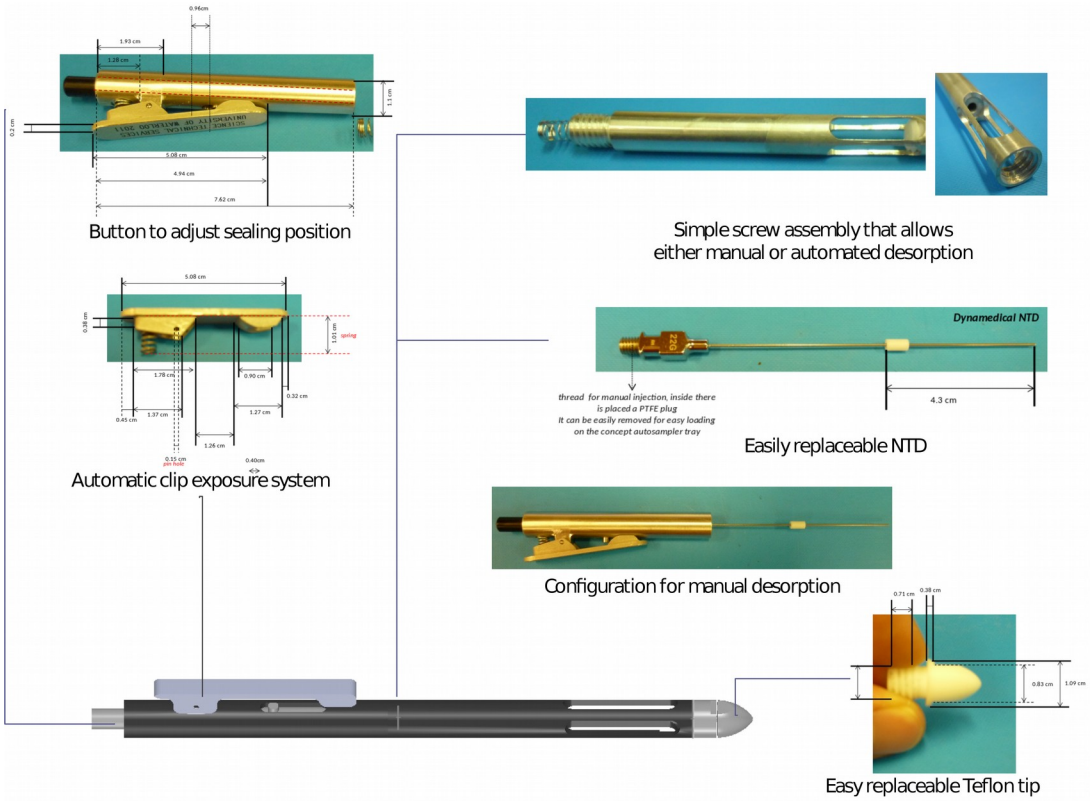


Figure SI-14

Schematic drawing of the new pen-like diffusive sampler for needle trap.

Figure SI-15

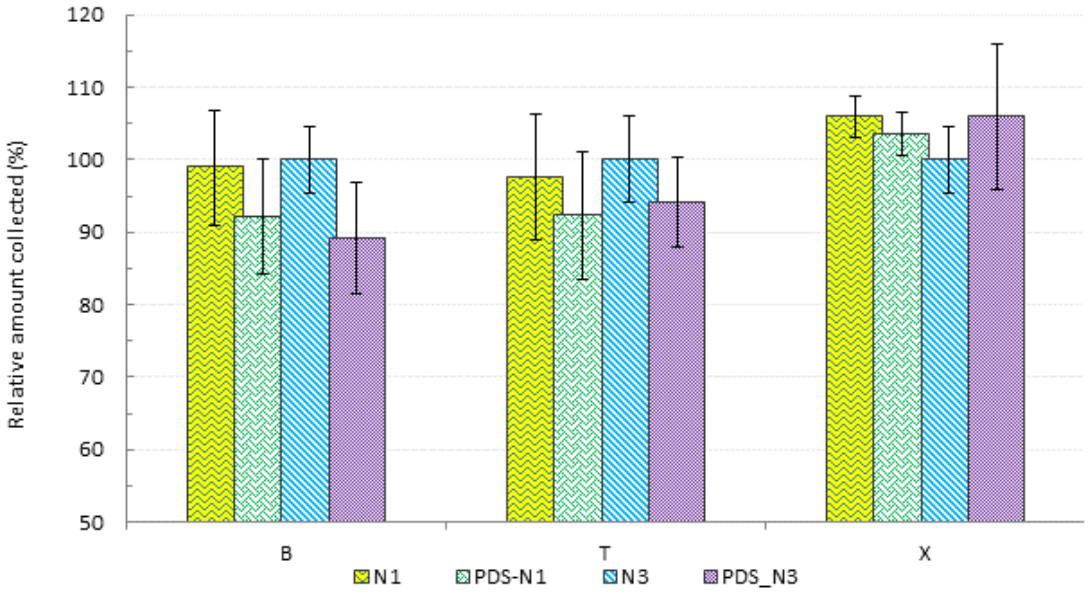


Figure SI-15 Evaluation of the effect of the pen-like diffusive sampler (PDS) on the uptake rate of two different NT pack with 1 cm of Car (Z=0.25 cm, t = 30 min, T= 25ºC). Error bars represent the standard deviation of the mean (n = 4).

Figure SI-16

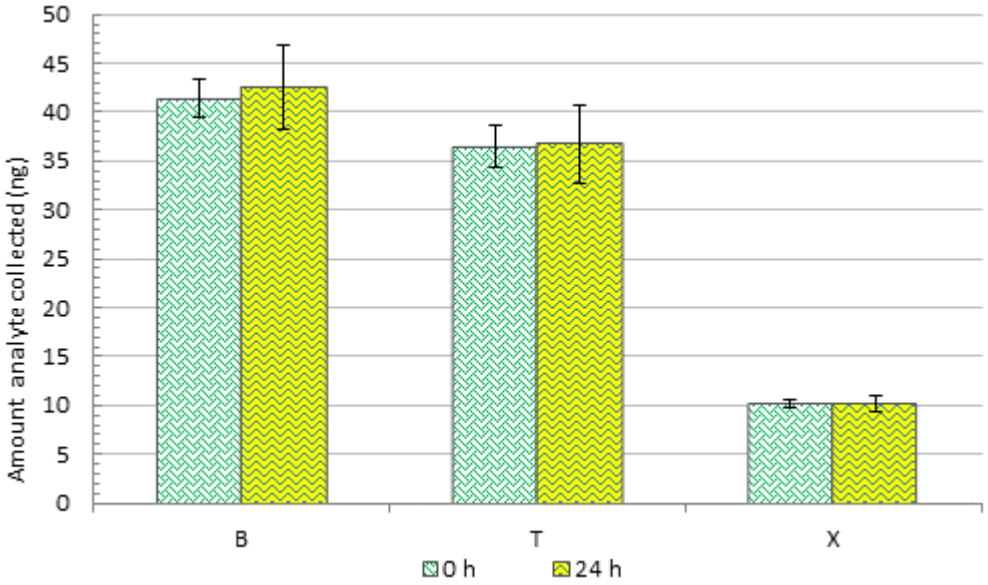


Figure SI-16 Storage stability of the pen-like diffusive sampler (PDS) containing a NT packed with 1 cm of Car (Z=0.25 cm, t = 30 min, T= 25ºC). Error bars represent the standard deviation of the mean (n = 3). Storage temperature = 23.5 ºC (room temperature).

Figure SI-17

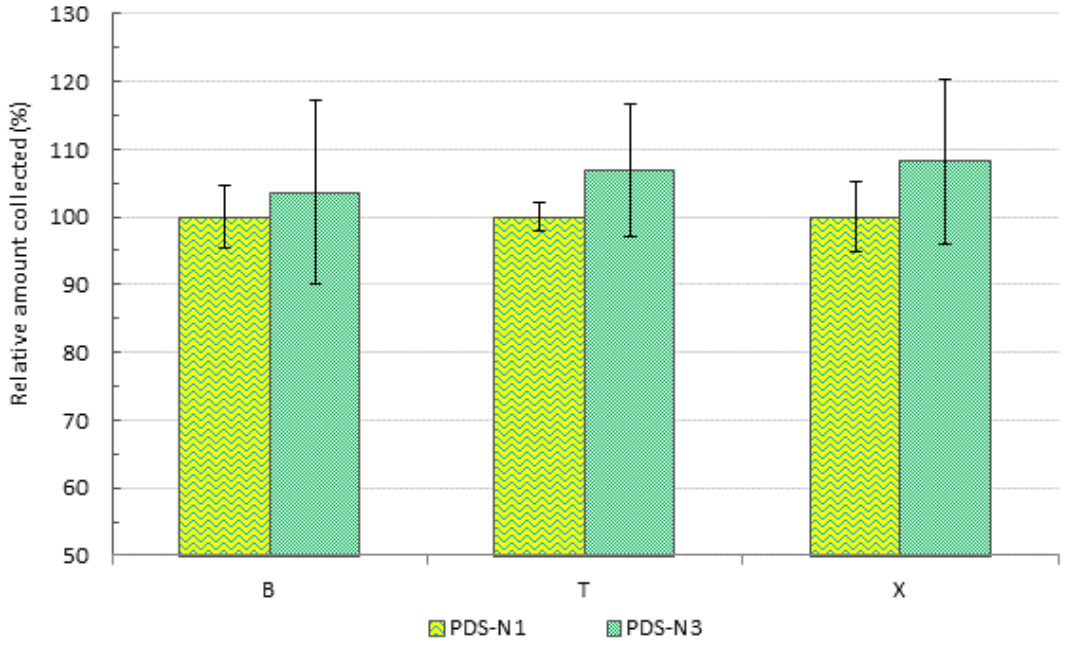


Figure SI-17 Evaluation of two pen-like diffusive samplers (PDS) using NT packed with 1 cm of CAR (Z=0.25 cm, t = 30 min, T= 25ºC). Error bars represent the standard deviation of the mean (n = 5).

Figure SI-18

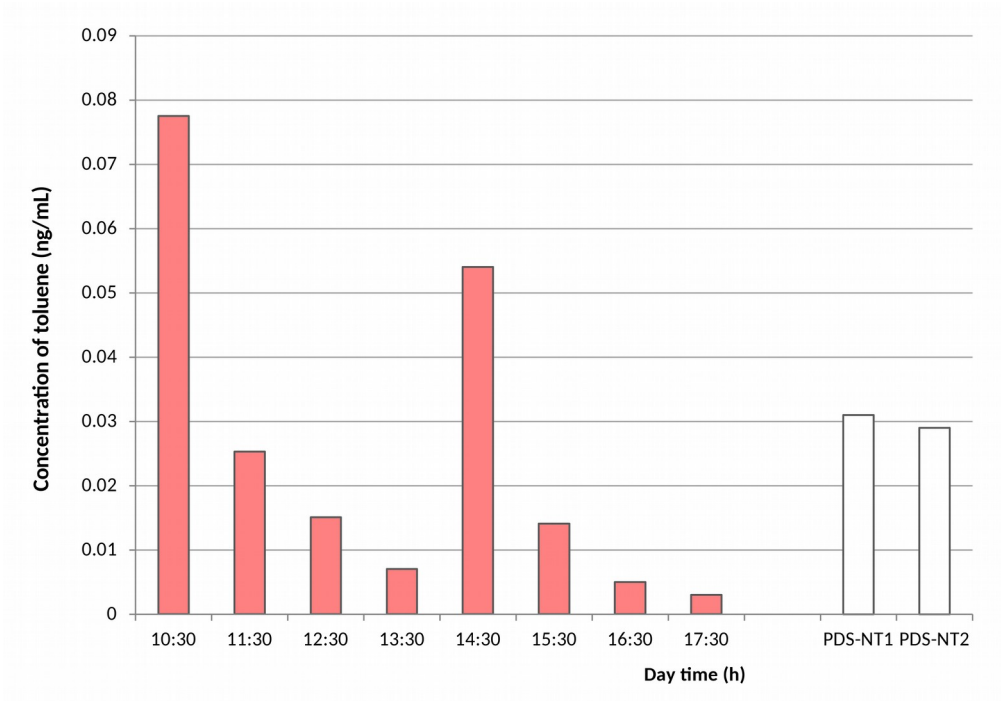


Figure SI-18.Concentration of toluene at different hours in a chemistry laboratory at University of Waterloo. TWA sampling was perform using PDS-NT using SGE NTs (Z=1 cm, t = 8 hours); Active sampling using a DVB (100 mL at 5mL/min).

Figure SI-19

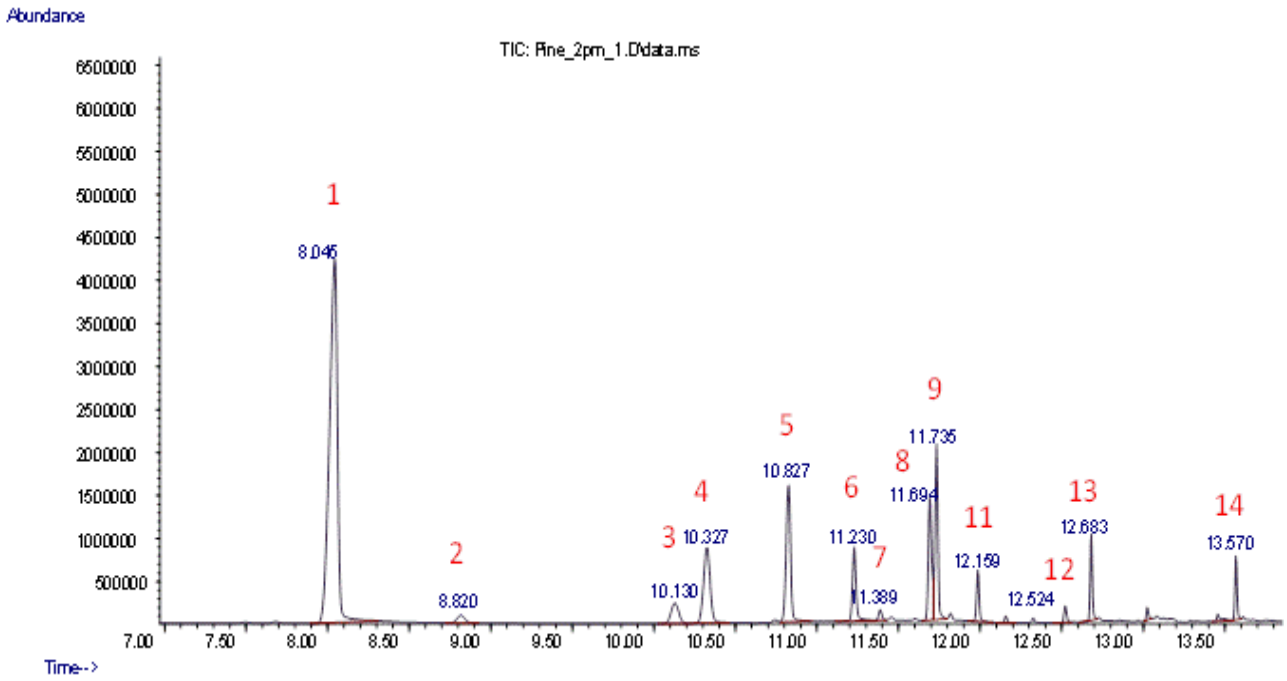


Figure SI-19 Typical GC-qMS profile of Pine treeBVOC after 30-s *in situ* sampling with a NT packed with DVB. Peak identity was included on Table 4.4.

List of Tables

Table SI-1. Statistical comparison of 9 commercial needle traps packed with 2 cm of DVB particles. F_{NT} is the F-ratio for the different treatments evaluated (different needle traps) and F_{crit} is the critical value of F for 27 experiments at a 95% level of confidence. RSD is the relative standard deviation for the inter-needle trap repeatability of 9 NTs (n=3) at 5 mL/min.

Compounds	F_{NT}	F_{crit}	RSD
Xylene	1.4		6.0
Decane	0.7	2.5	4.9
Limonene	1.0		6.3

Table SI-2

Compounds	**F_{NT}**	**F_{crit}**	**RSD**
Xylene	4.0		5.4
Decane	4.3	2.5	5.7
Limonene	4.0		5.2

Table SI-2 Statistical comparison of 9 commercial needle traps packed with 2 cm of DVB particles. $F_{NT}$is the F-ratio for the different treatments evaluated (different needle traps) and F_{crit} is the critical value of F for 27 experiments at a 95% level of confidence. RSD is the relative standard deviation for the inter-needle trap repeatability of 9 NTs (n=3) at 10 mL/min.

Table SI-3

Compounds	**F_{NT}**	**F_{crit}**
Toluene	3.0	5.1
Ethyl benzene	2.0	

Table SI-3 Statistical comparison of 3 commercial needle traps packed with 2 mm synthesized porous PDMS and 2 cm of Car particles at different flow rates. $F_{NT}$is the F-ratio for the different treatments evaluated (different needle traps) and F_{crit} is the critical value of F for 9 experiments at a 95% level of confidence. RSD is the relative standard deviation for the inter-needle trap repeatability of 1 NTs (n=3) at 2, 5, and 10 mL/min.

Table SI-4

Applications of Fick's Law
Sampling rate
TWA concentration determination
Sampling rate at different path
Sampler response time
Diffusion coefficient correction

Table SI-4 Equations that describe passive sampling analyte uptake in NT. n: mass of analyte loaded on the fibre or NT during the sampling time t; Dg: diffusion coefficient of the target analyte; A: area of the cross-section of the diffusion barrier; Cs: gas-phase analyte concentration at the coating position (sorbent bed); C_F: concentration of the analyte at the needle opening; SR: sampling rate; $SR_{(Z)}$: sampling rate at the position Z. $SR_{(Z')}$: sampling rate at the position Z'; D_g: Diffusion coefficient at 298 K; D_T: Diffusion coefficient at a different temperature, T (K); T: temperature

Table SI-5

Peak	t_R	$I_{(calc)}$	$I_{(lit)}$	Compound	CAS
1	8.045	933	936	α-pinene	7785-26-4
2	8.820	950	947	Camphene	79-92-5
3	10.130	978	978	Sabinene	3387-41-5
4	10.327	983	981	β-pinene	127-91-3
5	10.827	993	992	β-Myrcene	123-35-3
6	11.230	1007	1005	3-Hexen-1-ol, acetate, (E)-	3681-71-8
7	11.389	1017	1011	n-Hexyl acetate	142-92-7
8	11.694	1036	1032	Limonene	138-86-3
9	11.735	1039	1035	Eucalyptol	470-82-6
10	11.988	1055	1047	β-(E)-ocimene	3779-61-1
11	12.159	1066	1062	γ-terpinene	99-85-4
12	12.524	1090	1086	Terpinolene	586-62-9
13	12.683	1100	1098	Linalool	78-70-6
14	13.570	1200	1190	α-terpineol	98-55-5
15	14.503	1356	1351	α-terpineol acetate	80-26-2

16	14.753	1405	1405	Methyleugenol	93-15-2
17	14.947	1447	1419	Caryophyllene-E	87-44-5
18	15.227	1508	1480	Germacrene D	23986-74-5

Table SI-5 Experimental parameters used to determine the concentration α-pinene, β-pinene and limonene at different hours in pine trees. t_R, retention time (min); $I_{(calc)}$, retention index calculated; $I_{(lit)}$, retention index reported on the literature; CAS, CAS registry numbers[7].

Equation 1.

$$D_g = \frac{0.001 \times T^{1.75} \sqrt{1/M_{air} + 1/M_{VOC}}}{p \left(\sum V_{air} \right)^{1/3} + \left(\sum V_{VOC} \right)^{1/3}}$$

Where D_g is expressed in cm^2/s, T is the absolute temperature (K), M_{air} and M_{VOC} are molecular weights for air and the VOC of interest, p is the absolute pressure (atm), and V_{air} and V_{VOC} are the molar volumes of air and the VOC of interest (cm^3/mol)[8].

References

(1) Koziel, J. A.; Martos, P. A.; Pawliszyn, J. *J. Chromatogr. A***2004**, *1025*, 3–9.

(2) Zini, C. A.; Augusto, F.; Christensen, E.; Smith, B. P.; Caramão, E. B.; Pawliszyn, J. *Anal. Chem.***2001**, *73*, 4729–4735.

(3) Chen, Y.; Pawliszyn, J. *Anal. Chem.***2004**, *76*, 5807–15.

(4) Zhan, W.; Pawliszyn, J. *J. Chromatogr. A***2012**, *1260*, 54–60.

(5) Warren, J. M.; Pawliszyn, J. *J. Chromatogr. A***2011**, *1218*, 8982–8988.

(6) Warren, J. M.; Parkinson, D.-R.; Pawliszyn, J. *J. Agric. Food Chem.***2013**, *61*, 492–500.

(7) Kovats, E. *Helv. Chim. Acta***1958**, 1945.

(8) Fuller, E. N.; Schettler, P. D.; Giddings, J. C. *Ind. Eng. Chem.***1966**, *58*, 18.