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Nontargeted screening of air samples using TD-GC-HRMS to identify volatile compounds as markers of an industrial plant fire in Rouen, France

Tiffen Legeard^a, Séverine Tisse^a, Marie Vaccaro^a, Lamia Moufarrej^b, Mélanie Mignot^c, Clément Castilla^b, Isabelle Schmitz^b, Florence Portet-Koltalo^b, Clémence Méausoone^d, Christelle Monteil^d, Matthieu Fournier^e, Pascal Cardinael^{a,*}

^a Univ Rouen Normandie, FR3038, SMS, UR 3233, F-76000, Rouen, France

^b Univ Rouen Normandie, INSA Rouen Normandie, CNRS, Normandie Univ, COBRA UMR 6014, INC3M FR 3038, F-76000, Rouen, France

^c INSA Rouen Normandie, Univ Rouen Normandie, CNRS, Normandie Univ, COBRA UMR 6014, F-76000, Rouen, France

^d Univ Rouen Normandie, Université de Caen Normandie, ABTE, UR 4651, F-76000, Rouen, France

^e Univ Rouen Normandie, CNRS, Laboratoire M2C, UMR 6143 - Morphodynamique Continentale et Côtière, Place Emile Blondel, F-76821, Mont-Saint-Aignan Cedex, France

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ABSTRACT

An accidental industrial fire happened in Rouen (France) in september 2019 from a plant specialized in the production of mineral oils and engine additives. A few days after, passive sampling of the air was performed on thermodesorption tubes, from 09/30/2019 to 10/07/2019 using Tenax® TA and Carboxpack B&X sorbents. Two identical samplings were carried out 18 (2021) and 26 months (2022) after the fire in the same place to evaluate the urban and in-house background noises. Analyses were performed using a thermodesorption gas chromatograph coupled to a hybrid quadrupole Orbitrap mass spectrometer (TD-GC-Q-Orbitrap) in full scan mode. A nontargeted screening allowed to detect thousands of molecules (about 8000 on Tenax® TA and 3000 on Carboxpack B&X sorbents) including a large number of hydrocarbons, alkylbenzenes and polycyclic aromatic hydrocarbons in the tubes collected in 2019. But such hydrocarbons were not specific of the fire and then were not identified as industrial fire markers, as their presence were detected in the samples collected in 2021 and/or 2022. However, 22 sulfur-containing compounds were considered as potential markers because they were only detected in the samples collected in 2019 or at significantly higher level than in 2021 and/or 2022 and were detected in samples collected during Laboratory fire of engine oils. Moreover, these compounds were annotated with good confidence level. Among them, the identification of 6 sulfur-containing compounds, 2-acetylthiophene, 2-propionylthiophene, 2,2'-bithiophene, 3,3'-bithiophene, thieno [3,2-b]thiophene and di-tert-butyl-disulfide, and one oxygen-containing compound, 1,3,5-trioxane, was confirmed by injection of corresponding standards.

1. Introduction

More than 9511 tons of mineral oil containing additives for engines produced by the Lubrizol plant, and other materials stored by Normandie Logistique's plant close to Lubrizol, burned the September 26, 2019 in Rouen, Normandy, France (GPS coordinates: 49.436870, 1.061092). It was one of the largest industrial accidents in the 21st century in France. This fire produced a 22 km long black cloud of smoke. The fallout of soot was reported to occur up to 100 km away from the plant. Targeted air analyses were performed by governmental

organizations such as INERIS and AtmoNormandie and were published in the FRLUBRO014-R2 database, V1 (2020) and n°2520-001 (2020). However, only regulated compounds were reported in the official reports while numerous unknown compounds were released during the fire due to the combustion of very specific materials and products produced by Lubrizol or stored by the Normandie Logistique plant.

Many techniques have been developed to analyze urban air quality (Pristas, 1994; Helmig, 1999). Sampling air with adsorption tubes has proven to be a reliable technique and is described in many relevant regulations (NIOSH Method 2549, 1996; ASTM Method D-6196, 1997; ISO 16017-1, 2000). After sampling, thermal desorption-gas

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* Corresponding author. Université de Rouen Normandie, UFR Sciences & Techniques, SMS UR 3233, F-76000, Rouen, France.

E-mail address: pascal.cardinael@univ-rouen.fr (P. Cardinael).

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Abbreviations:

EIC	Extracted Ion Chromatogram
GC-Q-Orbitrap	Gas Chromatograph Coupled to a Quadrupole – Orbitrap Mass Spectrometer
PAH	Polycyclic Aromatic Hydrocarbon
HRMS	High Resolution Mass Spectrometry
RI	Retention Index
RHRMF	Reverse High-Resolution Mass Filter
RSI	Reverse Search Index
SI	Search Index
TD	Thermo-Desorption
TIC	Total-Ion Current

chromatography–mass spectrometry (TD-GC–MS) has been widely used for the analysis of volatile organic compounds (VOCs) and semivolatile organic compounds (SVOCs) due to its effectiveness, ease of implementation and reduced costs compared to those of other sampling techniques, such as canisters or Tedlar bags (Woelfenden, 1997; Vallecillos et al., 2019). Sampling air with sorbent tubes can be performed in two different ways: active sampling by pumping the air into the tube or passive sampling, which is based on the free flow of volatile molecules. Both techniques are described in ISO 16017–1:2000 and ISO 16017–2:2003 (ISO 16017-1, 2000; ISO 16017-2, 2003) for VOC analysis, respectively. Active air sampling using a pump has been widely used (Wong et al., 2013; US Environmental Protection Agency, 1999), but a sampling time of a few hours leads to episodic measurements, which are recommended to get a VOC temporal profile (Andrietta et al., 2010). Passive sampling is a good alternative for obtaining global concentration measurements because it can be performed over weeks of sampling, and large-scale simultaneous monitoring is possible (Skov, 2001; Huang et al., 2018).

Sorbent tubes can be filled with many different types of materials, such as porous polymers. Tenax® TA is the most commonly used for indoor monitoring of VOCs and SVOCs (Wolkoff, 1995) and is employed in the UK HSE and TO-1, TO-17 or IP-1B EPA methods (US Environmental Protection Agency, 1999; Harper, 2000; Huang et al., 2018). Despite its low surface density (35 m²/g), Tenax® TA has favorable properties for air sampling, for example, high breakthrough volumes of C₇ to C₂₆ (Lee et al., 2006). However, Tenax® TA is not suitable for correctly retaining compounds that exhibit low boiling temperatures (Harper, 2000; Klenø et al., 2002; Mastrogiacomo et al., 1995). Tenax® TA is stable up to 350 °C and can cause less bleeding and lower levels of impurities than its old homolog Tenax® GC. Several authors have studied the degradation of Tenax® TA exposed to reactive air pollutants (O₃, NO_x), and most have shown that benzaldehyde and acetophenone are the most significant artifacts (Rothweiler et al., 1991; Cao, 1994; Wolkoff, 1995; Lee et al., 2006), among other non-ramified or cyclic aldehydes and ketones, e.g., from pentanal to decanal, benzene, toluene, ethylbenzene, xylenes, phenylethyne, styrene, naphthalene, biphenyl, and phenol have also been reported as artifacts (Cao, 1994); and some authors found 2,6-diphenyl-*p*-benzoquinone (DPQ) and 2,6-diphenyl-*p*-hydroquinone (DPHQ) to be degradation products (Klenø et al., 2002; Clausen et al., 1997). Interestingly, Lee (Lee et al., 2006) observed that after a certain number of cycles of conditioning/exposure/analysis, concentrations of artifacts decreased until they disappeared. Alternatively, graphite black carbon (specifically Carboxpack B) has proven to be a good alternative to porous polymers for the environmental monitoring of very volatile compounds (Tolnai et al., 1999). Few studies have reported the degradation products of Carboxpack B, and Carboxpack X was shown to be the main degradation product after exposure to ozone (Lee et al., 2006). However, Carboxpack B produced alkenes, C₅ to C₁₀ linear aldehydes and a small amount of toluene.

Nontargeted environmental analysis requires analytical techniques allowing the detection of compounds at trace level and structural information to determine the possible chemical structures of emerging contaminants (Richardson, 2006). Gas chromatography coupled with high-resolution mass spectrometry (GC-HRMS) currently appears to be the most common technique for screening VOCs and SVOCs in the environment due to its high sensitivity; thus, GC-HRMS is the easiest method for characterizing compounds in the air (de Vos et al., 2011; Gomez-Ramos et al., 2019). Indeed, HRMS provides high mass accuracy, which allows determination of the exact mass-to-charge ratios (*m/z*) of the different ions and molecular formulas. In combination, spectrum comparison with spectral databases can increase the confidence of identification (Onghena et al., 2015), thus providing chemical structures. GC-Q-TOF is the most commonly used device for coupling GC and HRMS; however, only a few publications have reported the use of GC-Q-Orbitrap (Miralles et al., 2021), mainly because the technology is quite new and has been commercially available since 2015 (Mol et al., 2016). Nevertheless, its efficiency has been proven for both nontargeted (Hung et al., 2020; Remy et al., 2022) and targeted analyses in comparison to other analytical techniques, such as GC–MS/MS (Belarbi et al., 2021), GC–MS and GC-Q-TOF (Remy et al., 2021). So far, only one study has reported volatile and semi-volatile toxicants release during house fires, including phosphorus compounds and polycyclic aromatic hydrocarbons (PAHs) using GC–MS (Hewitt et al., 2017).

The main goal of this study was to identify unregulated molecules emitted during Rouen's industrial fire, as specific markers of this fire. Tenax® TA and Carboxpack B&X tubes were chosen for gas-phase passive sampling and were placed during one week in a building of the Rouen University, very close to the industrial plant (less than 2 km). Analyses were performed using a thermodesorption gas chromatograph coupled to a hybrid quadrupole Orbitrap mass spectrometer (TD-GC-Q-Orbitrap) in full scan mode. Peak annotation and confidence in these assignments were evaluated using the framework and scoring scheme (Koelmel et al., 2022). After that, two other identical samplings were carried out 18 and 26 months after the fire at the same place to evaluate the urban background noise and in-house background noise of the buildings and compare them to the sampling performed just after the industrial fire. Grubb's test was used to distinguish the molecules detected at significant higher concentrations in the sampling collected just after the industrial fire compare to urban and in-house background noise. A fire simulation in a laboratory combustion chamber was carried out with an oil mixture containing a high proportion of additives for engines. So, compounds annotated with high confidence in samples collected just after the industrial fire were searched in samples collected during the fire simulation to confirm their potential link with the industrial fire.

2. Materials and methods

2.1. Materials

Thermodesorption (TD) tubes packed with different adsorbents or mixture of adsorbents were used to sample the gas phase. The first one was packed with 200 mg of Tenax® TA (a porous polymer based on 2,6-diphenyl-*p*-phenylene oxide) particles with sizes in the range of 60–80 mesh. The second one was packed with 2.3 cm of Carboxpack B and 2.3 cm of Carboxpack X with a particle size in the range of 40–60 mesh. Both TD tubes had the following dimensions: 8.9 cm in length and 6.35 mm in width; these tubes were purchased from Gerstel (Mühlheim, Germany). Before sampling, each adsorbent tube was conditioned under a nitrogen flow of approximately 50 mL/min for 90 min at 280 °C for Tenax® TA and 330 °C for Carboxpack B&X. Tenax® TA was chosen for its ability to adsorb a wide range of compounds (from C₆ or C₇ to C₂₆ carbons in compounds), and graphite black carbon (half Carboxpack B and half Carboxpack X in cartridges) was used to adsorb molecules with a lower boiling point. Both sorbents were also selected for their low polarity, as they prevent humidity from affecting adsorption and desorption.

1,3,5-trioxane, 2-butylthiophene, 2-acetylthiophene, 2-propionylthiophene, 2,2'-bithiophene, 3,3'-bithiophene, thieno [3,2-b]thiophene and di-tert-butyl-disulfide were purchased from Tokyo Chemical Industry (TCI) Europe SA, Zwijndrecht, Belgium. TOTAL Quartz 9000 5 W40 motor oil and BARDHAL anti-wear hydraulic oil were purchased from Norauto (Barentin, France).

2.2. Analytical methods

The sorbent tubes were desorbed using a Multipurpose Sampler (MPS) (Gerstel, Mühlheim, Germany) connected to a gas chromatograph (Trace 1310, Thermo Scientific, Waltham, MA, USA) coupled with a hybrid quadrupole–Orbitrap mass spectrometer (Q Exactive, Thermo Scientific). An Elite-5MS GC column (60 m × 0.25 mm ID × 0.25 µm; PerkinElmer, Waltham, MA, USA) was used. The MPS was equipped with a thermal desorption unit (TDU; from Gerstel, Mühlheim, Germany), and a cold injection system (CIS) was used to cryofocus the analytes prior to their transfer into the capillary column. For this purpose, the TDU temperature was increased from 50 °C to 280 °C and 300 °C for the Tenax® TA and Carboxpack B&X tubes, respectively, at 120 °C/min. A split of 1:5 was applied for the tubes that collected emissions from the fire simulation. The compounds were then trapped at 5 °C in a CIS equipped with a glass liner packed with Tenax® TA. The cold trap was heated at 12 °C/min to 280 °C and held for 10 min, after which a split of 1:10 was applied.

Helium (purity >99.9999%, air liquide, Bagneux, France) was used as the carrier gas at a constant flow rate of 1.5 mL/min. The GC oven started at 40 °C, and after 4 min, the temperature was ramped to 300 °C at 8 °C/min and held at the final temperature for 5.5 min. The ion source was set at 250 °C, and electron ionization was performed at 70 eV. The data were acquired with the Thermo Scientific software Xcalibur in full scan mode (Total Ion Current) from m/z 50 to m/z 450 with 60,000 mass resolution (full width at half maximum (FWHM) measured at m/z 200). External mass calibration was performed using a

heptacosafuorotributylamine standard (FC 43, CAS 311-89-7), and internal mass calibration was performed using lock mass mode (m/z) ($C_3H_9Si^+$, 73.04680; $C_3H_9O_2Si_2^+$, 133.01356; $C_5H_{15}O_3Si_3^+$, 207.03235; $C_7H_{21}O_4Si_4^+$, 281.05114; $C_9H_{27}O_5Si^+$, 355.06993). For each batch of analysis, a corresponding blank for each support was previously analyzed.

The data were reprocessed using QualBrowser 4.1, TraceFinder 4.1 and Compound Discoverer 3.3 software (Thermo Scientific). The two last software programs were able to perform deconvolution and comparison with mass spectra and retention indices (RIs) collected from the NIST database (2.2, 2014) and in-Orbitrap spectral database (Thermo Fisher, 2015). To perform the RI calculations and for quality control, standard *n*-alkane mixtures of C_6 – C_{10} and C_{12} – C_{28} were injected under the same conditions. For Compound Discoverer software, the following parameters were used: mass tolerance = 5 ppm, S/N threshold = 3, RT tolerance = 5, and SI threshold = 500.

2.3. Samples collected after the industrial fire and for evaluation of urban and in-house background noises

A part of the Rouen university campus is located in the center of Rouen city (Pasteur campus, 1.35 km away from Lubrizol's plant, GPS coordinates: 49.443963, 1.077344) (Fig. 1). During the industrial plant fire, the wind was blowing northeast; thus, the cloud of smoke traveled just over the Pasteur campus of Rouen University, and fire ash and soot were deposited on the soil and surfaces of this campus.

Two locations on the Pasteur campus were chosen as sampling points inside the building: the first one was in an auditorium on the first floor (enclosed room) and the second one was on a walkway on the second floor (the air being more easily renewed). Four tubes (Tenax® TA and Carboxpack B&X) were placed for 1 week at the two sampling points (L-ROU-AIR-1, L-ROU-AIR-2, L-ROU-AIR-3 and L-ROU-AIR-4) (Table 1).

To compare the results with the usual urban background and in-house building noise, different samples were collected in April 2021

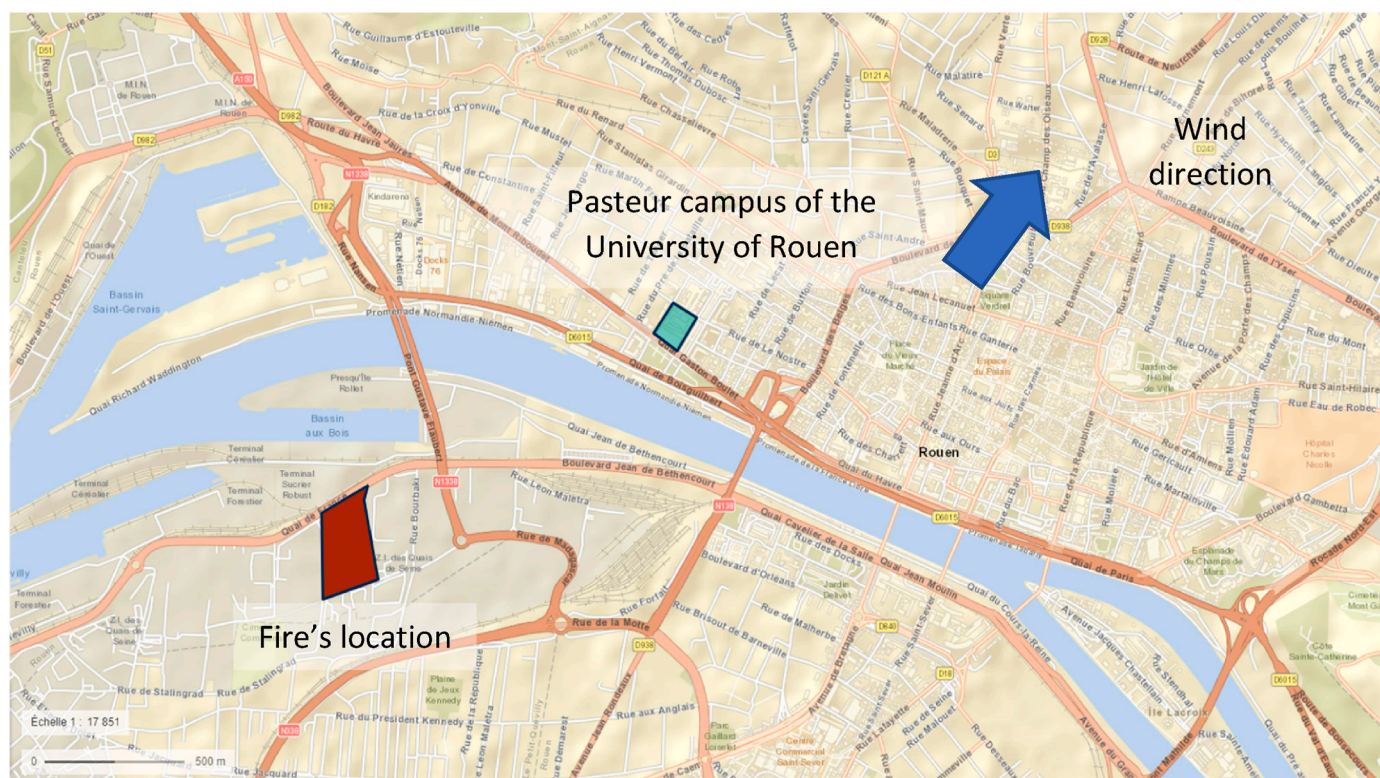


Fig. 1. Map of Rouen: fire location (GPS coordinates: 49.436870, 1.061092), wind direction and sampling site GPS (Pasteur campus, coordinates: 49.443963, 1.077344).

Table 1

Sampling conditions of the twelve L-ROU-AIR air samples (L = Lubrizol, ROU=Rouen).

Sample name	Phase	Sampling start	Sampling end	Location
L-ROU-AIR-1	Tenax® TA	09/30/2019, 9h am	10/07/2019, 14h30	Auditorium, 1st floor
L-ROU-AIR-2	Carbopack B&X			Walkway, 2nd floor
L-ROU-AIR-3				
L-ROU-AIR-4	Tenax® TA	04/02/2021, 9h am	04/09/2021, 16h45	Auditorium, 1st floor
L-ROU-AIR-5				
L-ROU-AIR-6	Carbopack B&X			Walkway, 2nd floor
L-ROU-AIR-7				
L-ROU-AIR-8	Tenax® TA	01/13/2022, 10h am	01/20/2022, 15h30	Auditorium, 1st floor
L-ROU-AIR-9				
L-ROU-AIR-10	Carbopack B&X			Walkway, 2nd floor
L-ROU-AIR-11				
L-ROU-AIR-12				

(L-ROU-AIR-5, L-ROU-AIR-6, L-ROU-AIR-7 and L-ROU-AIR-8) and January 2022 (L-ROU-AIR-9, L-ROU-AIR-10, L-ROU-AIR-11 and L-ROU-AIR-12). Sampling conditions were given in Table 1. The location, sampling time and adsorbent types were identical to those of the first sampling in 2019 just after the industrial fire.

About 500 molecules were detected in the blank tubes of Tenax®TA and Carbopack B&X. Blank tube analyses with the Tenax® TA liner showed the presence of benzene, toluene, xylenes, ethylbenzene, styrene, phenol, naphthalene, biphenyl, benzaldehyde, benzyl alcohol, benzothiazole, acetophenone and some alkanes and alkenes. Therefore, these compounds were not considered for the rest of the study except if the detected concentrations were significantly greater than those observed in the blank tube analysis (10 times higher).

The urban and in-house background noises were characterized with four samples using the two adsorbents: first in April 2021 (L-ROUEN-AIR-5, L-ROUEN-AIR-6, L-ROUEN-AIR-7, L-ROUEN-AIR-8) and the second in January 2022 (L-ROUEN-AIR-9, L-ROUEN-AIR-10, L-ROUEN-AIR-11, L-ROUEN-AIR-12). Grubbs's test is known as the extreme studentized deviate test and was used to detect one outlier in series of values. In the present case, this approach helped to determine if a chromatographic peak of a detected molecule, which seemed interesting, was significantly more intense in the tube collected in 2019 just after the industrial fire than in the tube placed in the same place in 2021 and 2022. The critical value was 1.749, as read in Grubbs' table for $n = 5$ samples (four from the samples collected in 2021 and 2022 and one from a 2019 sample presenting the highest intensity) for 99% confidence level. These values were compared to the results of the following calculation (Equation (1)):

$$(L - ROU - AIR - X - \mu) / \sigma \quad (\text{Equation 1})$$

where L-ROU-AIR-X is the sample collected in 2019 (see Table 1: Sampling conditions), μ is the mean of the 5 samples and σ is the standard deviation. The mean and standard deviation were calculated for the 5 samples. If the result was greater than 1.749 (value given in tables of critical values of Grubb's test), then the value from the 2019 sample was considered to be out of the urban and in-house background noises and possibly specifically linked to the accidental fire.

The spectra and retention indices (RIs) were compared to those of the NIST library. According to Koelmel (Koelmel et al., 2022), the

annotation confidence of the suggested molecules ranged from 1 to 5. The conditions for each confidence level are listed below.

- Level 1: Confirmed structure using an in-house library. The retention times were matched with those of standard databases generated in house using the same method, background matrix, and instrument. The retention times were within the RSD of the associated standards (no more than 1% deviation), and the reverse search index (RSI) was >600 with an in-house library.
- Level 2: Probable structure or close isomer using external libraries, that is, an RI match ($\Delta RI < 50$), an RSI >600 and a reverse high-resolution mass filter score (RHRMF) > 75.
- Level 3: Tentative candidate using an external library; matching spectra but no RIs specified in the library. SI > 500, RSI >600, RHRMF >75.
- Level 4: Chemical group or exact chemical formula.
 - o 4.a: Identification of unequivocal chemical formula. Exact mass matches for several fragments. In this paper, isomers were often found (one matching spectrum but several peaks in the chromatogram with the same fragments; thus, their identification confidence was 4.a).
 - o 4.b: Possible chemical series: unused in this study.
 - o 4.c: Possible chemical class (chemicals grouped based on structure, motif or similarity)
- Level 5: Unknown features. Does not fit any of the criteria for levels 1, 2, 3 or 4.

2.4. Samples collected during a laboratory simulated fire of oils containing engine additives

The fire conditions were reproduced as closely as possible in a combustion chamber (Montero et al., 2023), where 220 g of the TOTAL motor oil and 180 g of the BARDHAL anti-wear hydraulic oil were burned. A dilution of the air at the outlet of the combustion chamber (Fig. 2) was set up to 25 before collection of the gas phase in Tenax® TA and Carbopack B&X tubes. Quartz fiber filters (0.7 μm porosity) were placed upstream from the tubes to filter the particle phase. A pump connected to the tubes started to run 3 min after the beginning of the oil fire, and 10 L of air was sampled at a 375 mL/min flow rate. These experiments were performed in May 2022 in four replicates (Tenax® TA (LAB-EXP-T1, LAB-EXP-T2, LAB-EXP-T3 and LAB-EXP-T4) and Carbopack B&X (LAB-EXP-C1, LAB-EXP-C2, LAB-EXP-C3 and LAB-EXP-C4)).

3. Results and discussion

This study was focused on the identification of markers of the accidental industrial fire in the four samples collected from September 30, 2019 to October 7, 2019 just after the industrial fire, named L-ROUEN-AIR-1, L-ROUEN-AIR-2, L-ROUEN-AIR-3 and L-ROUEN-AIR-4 (Table 1). From this perspective, the inventoried stocks of products from the two plants helped to identify which atomic elements could be present, to be implemented in the QualBrowser 4.1 software. The GC-HRMS system used for this study has high mass accuracy (<3 ppm), allowing to use high resolution mass filters. Therefore, carbon, hydrogen, oxygen, sulfur, nitrogen and phosphorus were considered in this study. Moreover, silicon was added because compounds containing this atom can be released by GC stationary phase bleeding.

Therefore, a nontargeted strategy of identification was firstly employed on the four samples L-ROUEN-AIR-1, L-ROUEN-AIR-2, L-ROUEN-AIR-3 and L-ROUEN-AIR-4. As it was impossible to have air samples collected before the industrial fire to assess the urban background noise, eight samples were collected a long time after the fire, 18 and 26 months respectively, in the same place (L-ROUEN-AIR-5, L-ROUEN-AIR-6, L-ROUEN-AIR-7, L-ROUEN-AIR-8 and L-ROUEN-AIR-9, L-ROUEN-AIR-10, L-ROUEN-AIR-11, L-ROUEN-AIR-12). This allowed us to determine if an identified compound was significantly at higher

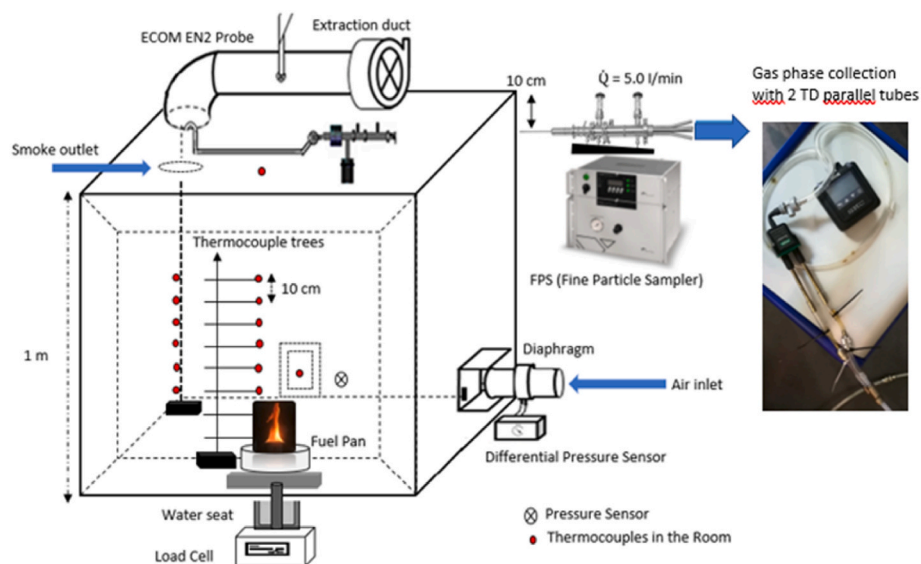


Fig. 2. Laboratory experimental setup of the combustion chamber, with the installation of two parallel TD tubes at the outlet for gas-phase sampling.

intensity in the samples collected just after the industrial fire compared to the samples collected 18 and 26 months after the industrial fire, using the Grubb test. Thus a global inventory of the compounds annotated on the tubes of samples ROUEN-AIR-1, L-ROUEN-AIR-2, L-ROUEN-AIR-3 and L-ROUEN-AIR-4 was performed allowing to detect more than 3000 compounds on Carbo-pack B&X tubes (L-ROUEN-AIR-3 and L-ROUEN-AIR-4), and approximately 8000 on Tenax®TA (ROUEN-AIR-1, L-ROUEN-AIR-2). Moreover, the presence of molecules containing heteroatoms were found in significantly greater proportions in 2019 just after the accidental fire than in the same place in 2021 and 2022.

The second part of this work consisted of a targeted research of the molecules identified in the samples collected just after the industrial fire in 2019, in samples collected during laboratory combustion experiments of commercial oils containing engine additives (LAB-EXP-T1, LAB-EXP-T2, LAB-EXP-T3, LAB-EXP-T4, LAB-EXP-C1, LAB-EXP-C2, LAB-EXP-C3 and LAB-EXP-C4), to confirm that they could be actually considered as markers of the accidental fire.

3.1. Compounds detected in the air collected just after the industrial fire

In the two industrial plants, the products stored were mainly mineral oils, with or without additives, or additive formulations (List of burned products, 2021). Mineral oils contain a lot of alkane isomers and aromatic compounds. Additives may also contain many isomers, as they result from the synthesis of products containing mixtures of alkyl chain isomers. Examples of additives produced in the Lubrizol plant that may have been burned can be cited to highlight the diversity of compounds. Additives could contain various heteroatoms such as nitrogen (reaction products of benzeneamine, *N*-phenyl- with nonene (branched); diphenylamine; (*Z*)-octadec-9-enylamine, C₁₆-C₁₈-alkylamines), oxygen (phenol, dodecyl-, branched; C₁₄-C₁₈ alpha-olefin epoxide, reaction products with boric acid; benzenepropanoic acid, 3,5-bis(1,1-dimethyl-ethyl)-4-hydroxy-, C₇-C₉-branched alkyl esters), sulfur (calcium branched alkyl phenate sulfide; polysulfides, di-*tert*-butyl) and phosphorus (dibutyl phosphonate; triphenyl phosphite) and compounds with several heteroatoms (derived from phosphorodithioic acid; *O,O,O*-triphenyl phosphorothioate; reaction products of 4-methyl-2-pentanol and diphosphorus pentasulfide; propoxylated, esterified with diphosphorus pentoxide, and salted by amines, C₁₂-C₁₄-*tert*-alkyl). Therefore, the additives may have volatilized without transformation during the fire due to high temperatures but also, the combustion of these products could have resulted in the formation of a large variety of other

compounds, including numerous isomers. Approximately 3000 molecules were detected on Carbo-pack B&X tubes (L-ROUEN-AIR-3 and L-ROUEN-AIR-4), and approximately 8000 were detected on Tenax®TA (ROUEN-AIR-1, L-ROUEN-AIR-2) via a deconvolution process implemented in Compound Discoverer 3.3 software; these molecules were compared to the approximately 500 molecules detected in the blank tubes of Tenax®TA and Carbo-pack B&X. However, approximately one-third of the spectra was not attributed due to coelution of compounds or because the mass spectra were not available in the NIST database. So finally, about a total of 5000 peaks were annotated.

The 18 molecules presenting the most intense signal from the Tenax® TA (ROUEN-AIR-1, L-ROUEN-AIR-2) with an intensity superior to 10⁸ and Carbo-pack B&X (L-ROUEN-AIR-3 and L-ROUEN-AIR-4) tubes with an intensity superior to 10⁷ are presented with putative annotations in the supplementary data (Tables S1 and S2), which mostly include hydrocarbons and oxygen-containing compounds. Only 3 peaks were not annotated. As expected, numerous alkylbenzene derivatives, one phenol derivative and one alkyldiol derivative that could have been emitted during the fire were identified. These results were in accordance with the targeted analyses performed by AtmoNormandie and INERIS (FRLUBRO014-R2 database, V1 (2020) and n°2520-001 (2020)) just after the Lubrizol and Normandie Logistique plant fire. Nevertheless, alkanes, alkenes, and aromatic hydrocarbons are known to be present in the environment because these compounds are commonly emitted from vehicles and industrial plants, particularly near dense urban and industrialized areas (Huang et al., 2020; Cordell et al., 2021). Consequently, none of the hydrocarbon molecules could be referenced as a marker of Lubrizol and Normandie Logistique plant fire. However, interestingly, among the C_xH_y compounds, a large majority of identified molecules in the chromatograms were aromatic compounds (alkylbenzenes, PAHs). For example, the C₉H₇⁺ ion (*m/z* 119.0855), characteristic of alkylbenzene derivatives, was largely present in the air samples from 2019 (L-ROUEN-AIR-1, L-ROUEN-AIR-2, L-ROUEN-AIR-3 and L-ROUEN-AIR-4) but also in those from the simulated fire (LAB-EXP-T1, LAB-EXP-T2, LAB-EXP-T3 and LAB-EXP-T4, LAB-EXP-C1, LAB-EXP-C2, LAB-EXP-C3 and LAB-EXP-C4). To illustrate this, EIC chromatograms are presented in Fig. 3. However, these EIC chromatograms obviously differ significantly, not only because of the difference in the quality of the air sampled just after the real fire or during the simulated fire, but also because of the difference in the burned oils. The diversity of mineral oils, engine additives and materials burned during the accidental fire was considerably higher. On the chromatograms of samples L-ROU-1,

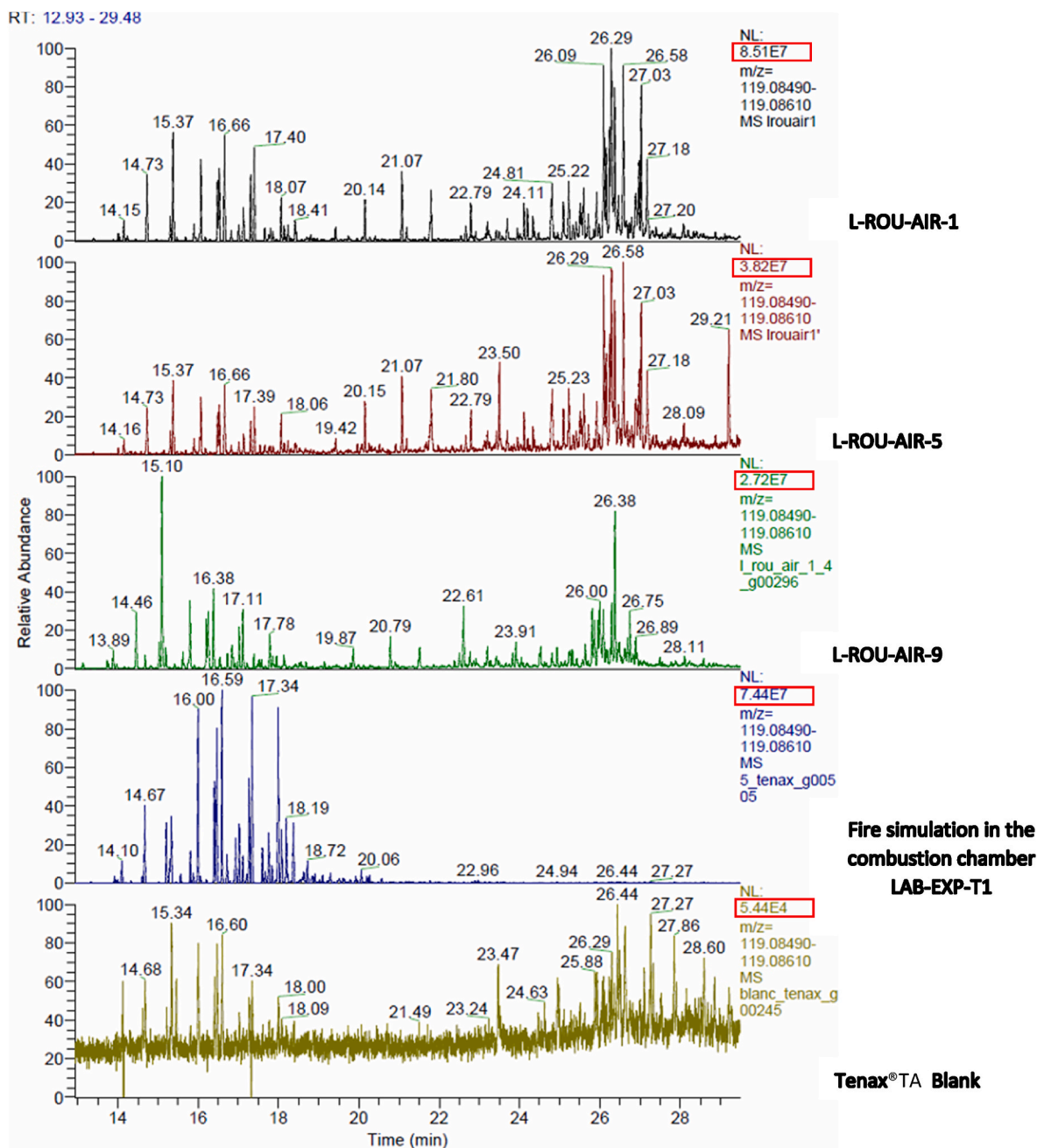


Fig. 3. EIC chromatograms of m/z 119.0855 $C_9H_{11}^+$ ion. From the top to the bottom: L-ROU-AIR-1 (2019 sampling); L-ROU-AIR-5 (2021 sampling); L-ROU-AIR-9 (2022 sampling); laboratory fire simulation LAB-EXP-T1 (2022 -experiment); Tenax® TA Blank. Note the maximum peaks intensity at the right of each chromatogram (framed in red).

L-ROU-5, and L-ROU-9, some peaks were observed between 25 and 30 min corresponding to oxygenated and aliphatic compounds which were not observed on LAB-EXP-T1. It can be noticed that the $C_9H_{11}^+$ ion was also present in the samples collected in 2021 and 2022 (L-ROUEN-AIR-5, L-ROUEN-AIR-6, L-ROUEN-AIR-7, L-ROUEN-AIR-8 and L-ROUEN-AIR-9, L-ROUEN-AIR-10, L-ROUEN-AIR-11, L-ROUEN-AIR-12 respectively) but with weaker intensities, which were decreasing from 2019 to 2022. Finally, some of the most intense C_xH_y compounds found in the air after the accidental fire were also among the most intense in the samples obtained after the simulated fire in the combustion chamber (LAB-EXP-T1, LAB-EXP-T2, LAB-EXP-T3 and LAB-EXP-T4, LAB-EXP-C1, LAB-EXP-C2, LAB-EXP-C3 and LAB-EXP-C4): namely, 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene, 1,3-dimethylbenzene, 1-ethyl-2-methylbenzene, mesitylene, 1-ethyl-2,4-dimethylbenzene and 1,2,3,

4-tetramethylbenzene.

Some oxygen-containing compounds, namely, dibutyl phthalate, *p*-decylphenol, 1,10-decanediol, 2-phenoxyethanol, menthol, eucalyptol, and 2-ethoxy-2-methylpropane, were found in similar amounts in 2019, 2021 and 2022 ((ROUEN-AIR-1, L-ROUEN-AIR-2, L-ROUEN-AIR-5, L-ROUEN-AIR-6 and L-ROUEN-AIR-9, L-ROUEN-AIR-10). Hence, they could not be specifically linked to the accidental fire and can be considered part of the urban or in-house air background noises. Finally, supplementary material's Tables (S1 and S2) display two compounds found in Carbopack B&X, both containing a sulfur atom, which are possibly of interest and will be discussed later.

3.2. Focus on molecules containing heteroatoms as suspected markers

This section is dedicated to the identification of molecules containing heteroatoms that were found in significantly greater proportions (Grubb's test value > 1.749) in 2019 just after the accidental fire (L-ROUEN-AIR-1, L-ROUEN-AIR-2, L-ROUEN-AIR-3 and L-ROUEN-AIR-4) than in the ambient air in 2021 and 2022 (L-ROUEN-AIR-5, L-ROUEN-AIR-6, L-ROUEN-AIR-7, L-ROUEN-AIR-8 and L-ROUEN-AIR-9, L-ROUEN-AIR-10, L-ROUEN-AIR-11, L-ROUEN-AIR-12 respectively). So, these compounds appeared interesting as potential markers of the industrial fire.

The results were separated according to the collecting adsorbents (Tenax® TA and Carbopack B&X, (L-ROUEN-AIR-1, L-ROUEN-AIR-2 and L-ROUEN-AIR-3, L-ROUEN-AIR-4 respectively)), and the proposed annotations at the highest levels 1 and 2 are reported in Tables 2 and 3, respectively (lower levels of identification, 3 and 4, are reported in Tables S3 and S4, respectively). Even if some molecules, such as trioxane, dioxane derivatives and benzofuran derivative, were detected in different tubes (L-ROUEN-AIR-1, L-ROUEN-AIR-2, L-ROUEN-AIR-3, L-ROUEN-AIR-4), to avoid repetition, only the result for the adsorbent showing the highest area for a given molecule was reported in Tables 2 and 3. Thus, a total of 6 oxygen-containing compounds, considered as suspected markers, including trioxane and dioxane derivatives, and two sulfur-containing compounds (bisulfide and trisulfide) presented the highest intensities on Tenax® TA tube and were annotated. Also 34 sulfur-containing compounds including thiophene derivatives and 1 oxygen-containing compound (benzofuran derivative) presented the highest intensities on Carbopack B&X.

To confirm a possible link between the presence of these compounds in the gas phases of 2019 and from the simulated fires of oils containing engine additives, a comparison between these identified molecules was done using similar data processing methods and a targeted analysis strategy. The results are presented in Table S5. Among the 35 sulfur-containing molecules detected (Tables 2, 3, S3 and S4) in the gas phase after the industrial fire of 2019, 34 molecules were also detected on the adsorbent tubes that collected the air during the fire simulation. The orders of magnitude of peak areas were sometimes very different due to the difference in composition of oil additives from Lubrizol production burned in 2019 and the bought commercial engine oils burned in 2022 in the laboratory combustion chamber. Nevertheless, the detection of compounds involved in the gas-phase emission of the fire reproduced in the laboratory appeared an important element, allowing us to conclude that the molecules listed in Table S5 can be linked to the industrial fire. Among them, 6 (2-acetylthiophene, 2-propionylthiophene, 2,2'-bithiophene, 3,3'-bithiophene, thieno [3,2-b]thiophene and di-tert-butyl-disulfide) were annotated on the chromatograms obtained from the Carbopack B&X tube with the highest level 1 of confidence, by injection of the corresponding standards. Moreover, di-tert-butyl-disulfide was also detected by AtmoNormandie and was present in Lubrizol's stock as di-tert-butyl polysulfide. A total of 15 compound annotations remained at level 2 because standards could not be injected. Concerning oxygen-containing molecules, 1,3,5-trioxane was annotated with the level 1 from the air collected in 2019, but was not identified in the sample collected during the fire simulation. However, it may have

been produced by the combustion of other stocked products from Lubrizol and Normandie logistique plants.

To summarize, 21 organic sulfur-containing compounds and 1 oxygen-containing molecule annotated with the levels 1 or 2 of confidence were suggested as volatile or semi-volatile nonregulated markers of the accidental fire, disseminated in the air. The main limitation of this work was that no internal standard could be used during 2019 sampling, which made it impossible to accurately quantify the compounds emitted during the industrial fire. However, the identification of molecules remains of primary importance for evaluating the unknown or unregulated molecules emitted during this special fire, and their possible subsequent release into the environment.

4. Conclusion

After an important accidental industrial fire, passive sampling tubes with different sorbents were placed next to the combustion source, and the ability of these tubes to collect a large range of VOCs and SVOCs from the gas phase was demonstrated. TD-GC-HRMS in full scan mode appeared to be a powerful technique for identifying non-targeted molecules and non-regulated molecules, which are generally not suspected and detected by air-controlling organisms. So, 35 sulfur-containing compounds were considered as potential markers because they were only detected in the samples collected in 2019 or at significantly higher level than in 2021 and/or 2022, and were annotated with good confidence level regarding the suggested structures 2-acetylthiophene, 2-propionylthiophene, 2,2'-bithiophene, 3,3'-bithiophene, thieno [3,2-b]thiophene and di-tert-butyl-disulfide, were identified as markers of the accidental fire from the Lubrizol and Normandie Logistique's plants with the best level of confidence (level 1) by injection of standards. The latter has also been detected by AtmoNormandie and was present in Lubrizol's stock as di-tert-butyl polysulfide. The same compounds were also clearly identified in the gas-phase emission of a controlled fire with mixtures of engine oils burned in a laboratory combustion chamber. Moreover, 15 other sulfur-containing compounds were annotated with the level 2 of confidence. Many other compounds have also been found at levels 3 and 4 of identification, that is, their structural formula remains uncertain. Moreover, this study demonstrated that many sulfur-containing compounds were released into the air in the vapor-phase during the industrial fire and some days after it. One oxygen-containing compound, 1,3,5-trioxane, could also be retained as marker. Finally, the dispersion of these markers into the environment might be of interest for studying their persistence over time. It could also be relevant to specifically look for those compounds in environmental matrices such as soil, natural water and sediments.

CRedit authorship contribution statement

Tiffen Legeard: Writing – original draft, Visualization, Formal analysis. **Séverine Tisse:** Writing – review & editing, Supervision, Methodology, Data curation. **Marie Vaccaro:** Software, Formal analysis. **Lamia Moufarrej:** Writing – review & editing, Methodology, Data curation. **Mélanie Mignot:** Writing – review & editing, Methodology. **Clément Castilla:** Methodology, Formal analysis, Data curation.

Table 2

Remarkable molecules identified in Tenax® TA tubes (L-ROUEN-AIR-1 and L-ROUEN-AIR-2, Grubb's test value > 1.749).

Main ions of the MS spectra: <i>m/z</i> ratios (uncertainty in ppm) by decreasing intensity	Intensity of the most abundant ion	Name suggestion	Molecular formula	RI (sample)	Δ RI	Grubb's test value	SI/RSI	RHRMF	Level of confidence (Koelmelet al., 2022)
89.02333 (0.5 ppm) 61.0284 (0.9 ppm)	4.10 ⁷	1,3,5-trioxane	C ₃ H ₆ O ₃	682	6	1.765	840/ 840	99.4	1
57.0699 (0.4 ppm) 178.0843 (-0.8 ppm) 122.0218 (-0.5 ppm)	3.10 ⁵	di-tert-butyl-disulfide	C ₈ H ₁₈ S ₂	1137	2	1.789	n.d. ^a	n.d. ^a	1

^a n.d. = not detected by Compound Discoverer 3.3 software.

Table 3

Remarkable molecules identified in Carbopack B&X (L-ROUEN-AIR-3 and L-ROUEN-AIR-4), Grubb's test value > 1.749).

Main ions of the MS spectra: <i>m/z</i> ratios (<i>uncertainty in ppm</i>) by decreasing intensity	Area of the most abundant ion	Name suggestion	Molecular formula	RI (sample)	Δ RI	Grubb's test value	SI/RSI	RHRMF	Level of confidence (Koelmel et al., 2022)
84.0029 (0.4 ppm)	2.10 ⁷	thiophene	C ₄ H ₄ S	664	11	1.788	852/867	91.4	2
57.9872 (1.0 ppm)									
97.0106 (0.1 ppm)	6.10 ⁶	2-methylthiophene	C ₅ H ₆ S	775	0	1.771	909/909	99.4	2
98.0184 (-0.3 ppm)									
97.0107 (0.0 ppm)	2.10 ⁷	3-methylthiophene	C ₅ H ₆ S	783	3	1.788	898/899	99.1	2
98.0184 (-0.4 ppm)									
97.0107 (0.1 ppm)	4.10 ⁶	3-ethylthiophene	C ₆ H ₈ S	873	4	1.787	883/885	99.4	2
112.0341 (0.0 ppm)									
97.0107 (0.2 ppm)	2.10 ⁶	3,4-dimethylthiophene	C ₆ H ₈ S	885	3	1.788	829/833	84.2	2
111.0263 (-0.1 ppm)									
112.0341 (0.0 ppm)									
97.0107 (0.3 ppm)	6.10 ⁵	2,3-dimethylthiophene	C ₆ H ₈ S	897	1	1.784	873/878	96.7	2
111.0263 (-0.0 ppm)									
112.0341 (0.4 ppm)									
97.0107 (0.3 ppm)	1.10 ⁸	2-butylthiophene	C ₈ H ₁₂ S	1085	9	1.789	830/834	99.1	2
140.0653 (-0.7 ppm)									
97.0107 (0.2 ppm)	1.10 ⁷	2-pentylthiophene	C ₉ H ₁₄ S	1175	6	1.785	817/830	98.2	2
154.0811 (0.1 ppm)									
97.0107 (0.3 ppm)	6.10 ⁶	2-hexylthiophene	C ₁₀ H ₁₆ S	1278	1	1.751	704/751	98.8	2
168.0967 (0.4 ppm)									
110.9899 (-0.1 ppm)	6.10 ⁶	3-thiophene-carboxaldehyde	C ₅ H ₄ OS	1002	1	1.781	855/866	88.9	2
111.9977 (-0.2 ppm)									
110.9899 (-0.1 ppm)	1.10 ⁷	2-thiophene-carboxaldehyde	C ₅ H ₄ OS	1013	6	1.774	842/851	98.6	2
111.9977 (-0.3 ppm)									
110.9899 (0.3 ppm)	7.10 ⁶	2-acetylthiophene	C ₆ H ₆ OS	1107	8	1.768	626/756	96.7	1
126.0134 (0.0 ppm)									
110.9899 (0.2 ppm)	3.10 ⁶	2-propionylthiophene	C ₇ H ₈ OS	1201	9	1.784	n.d. ^a	n.d.	1
140.0290 (-0.2 ppm)									
165.9904 (-0.6 ppm)	7.10 ⁵	2,2'-bithiophene	C ₈ H ₆ S ₂	1426	9	1.782	634/785	85.5	1
121.0107 (0.2 ppm)									
165.9904 (-0.6 ppm)	1.10 ⁵	3,3'-bithiophene	C ₈ H ₆ S ₂	1465	7	1.789	n.d. ^a	n.d.	1
121.0107 (0.2 ppm)									
139.9748 (0.2 ppm)	3.10 ⁶	thieno [3,2-b]thiophene	C ₆ H ₄ S ₂	1229	5	1.777	841/928	99.2	1
96.0028 (0.2 ppm)									
125.0056 (0.1 ppm)	5.10 ⁵	5-methyl-2-thiophene-carboxaldehyde	C ₆ H ₆ OS	1104	14	1.788	506/862	79.4	2
126.0134 (0.1 ppm)									
97.0107 (0.3 ppm)	5.10 ⁶	3-methyl-2-thiophene-carboxaldehyde	C ₆ H ₆ OS	1136	15	1.777	675/783	98.9	2
125.0056 (0.1 ppm)									
126.0134 (0.1 ppm)	6.10 ⁶	1-(4-methyl-2-thienyl)ethanone, and isomers	C ₇ H ₈ OS	1223	17	1.783	729/730	94.8	2
97.0107 (0.3 ppm)									
125.0056 (0.1 ppm)	2.10 ⁶		C ₇ H ₈ OS	1231	9	1.775	771/787	99.6	2
140.0290 (-0.4 ppm)									
97.0107 (0.2 ppm)	2.10 ⁶	4,5,6,7-tetrahydro-3,6-dimethyl-benzofuran	C ₁₀ H ₁₄ O	1180	15	1.787	808/818	99.8	2
108.0569 (-0.2 ppm)									
150.1038 (-0.6 ppm)									

^a n.d. = not detected by *Compound Discoverer 3.3 software*.

Isabelle Schmitz: Writing – review & editing, Methodology. **Florence Portet-Koltalo:** Writing – review & editing, Project administration, Methodology. **Clémence Méausoone:** Formal analysis. **Christelle Monteil:** Writing – review & editing. **Matthieu Fournier:** Project administration, Funding acquisition. **Pascal Cardinael:** Writing – review & editing, Validation, Supervision, Methodology, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Pascal Cardinael reports financial support was provided by French National Research Agency. Tiffen Legeard, Severine Tisse, Marie Vaccaro, Lamia Moufarrej, Melanie Mignot, Clement Castilla, Isabelle Schmitz, Florence Portet-Koltalo, Clemence Meausoone, Christelle Monteil, Matthieu Fournier reports financial support was provided by French National Research Agency. Pascal Cardinael reports financial support

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Appendix A. Supplementary data

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