

# Use of Chemical Signature to Trace the Impact of Emission Sources

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## Research Article

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# Abstract

The composition of organic fraction associated to particulate emissions depends on their nature as well as on contour conditions. Therefore, many Authors have investigated the chemical signature of airborne particulate matter and dusts with the goal of identifying the pollution sources and assessing their impact on the environment and health. Usually, Authors use three complementary tools for this goal; they are specific source markers, concentration ratios of pairs of congeners, and percent distributions of homologues within a group. After the presentation of the state-of-the-art about non-polar aliphatic (alkanes and alkenes), aromatic (PAHs, Nitro-PAHs) and polar (fatty acids, organic halides, polysaccharides) compounds associated to emissions, this paper provides new information with regard to chemical signature non-polar fraction, suitable to trace the impact of sources on airborne particulate matter and settled dust. Non-polar organic fraction comprises short/medium-chain alkenes and alkanes (with carbon numbers ranging from 12 to 23), which display distinct relative abundances in petrol-derived exhausts, microorganism residues and high vegetation leaf debris. Meanwhile, long-chain alkanes associated to tobacco smoke show a peculiar iso/anteiso/normal homologues fingerprint as well as *n*-hentriacontane percentages higher than other emissions. Based on this particular alkane distribution, two indexes (ATSR and AICR) have tentatively identified and tested though comparing their rates in some sets of particulate samples. Until now, the study of molecular signature has overall limited to qualitative purposes and seldom exploited to achieve quantitative estimates of contributions of sources to air pollution. Future investigations will reach this goal through further clarifying the nature and behavior of organic contaminants associated to airborne and settled particulate matters.

## 1. Introduction

The release of toxicants in the atmosphere has recognized to induce harmful effects on humans and injure the environment. Therefore, the knowledge of nature, amount and land spread of emissions appears mandatory if strategies aimed at mitigating the toxicants impact must be implemented [Albaiges et al 1984, Bascom et al 1996, Yassaa et al 2001, Ma et al 2015, Błaszczuk et al 2017, Sifakis et al 2017, Cetin et al 2018, Nieder et al 2018, Vaz 2018]. Chemical and physical characterization of gas and particulate phases plays a key role to picture the aftermaths of pollutants release into the environment (i.e., through valuing the concentrations of selected chemicals in air and exhausts and comparing them with current legislation). Besides, it allows assessing the relative importance of sources that affect the site or land domain which is under study [Gundel et al 1993, Hecht 1999, Ventrice et al 2013, Jedynska et al 2014, Giulivo et al 2016, Liu et al 2017, Praveena et al 2018, Rabhi et al 2018, Yuri et al 2018, Brehmer et al 2020].

At this regard, organic substances associated to particulate matter (both aerosols and dust settled on surfaces and soil) are important tools of investigation and at the same time subjects of scientific challenge, due to their complexity and variety. Organic substances are classified in a number of groups displaying very different properties like acidity/alkalinity/neutrality, grade of polarity, water and n-octanol solubility, vapor pressure, inertness vs. oxidants and light- They are linear and cyclic aliphatic

compounds, polycyclic aromatic hydrocarbons, acids, amines, carbonyls, halides, organic sulfates and phosphates, etc.. Many of them, as peculiarly associated to sources, have identified as tracers of living organisms, natural phenomena and man's activities.

Unfortunately, only in a handful of happy cases one substance is unequivocally typical of one emission, so that it allows revealing and even valuing the impact of that source on the environment. More frequently, many chemicals are associated to many emissions, and the compound peculiarity is missed, nevertheless, in this case the composition per groups and the distribution pattern of congeners within organic groups can aid in the goal of identifying the pollution sources. For instance, biofuels are usually richer of esters than fossil fuels, and the opposite occurs for polycyclic aromatic hydrocarbons (PAHs) [Damanik et al 2018]. Besides, the percentages of PAHs associated to ultra-fine, fine and coarse fractions of suspended particulate change with the nature of source [Zielinska et al 2004]. Fresh exhausts are prone to action of light (overall UV) and oxidizing species ( $O_3$ ,  $NO_2$ , OH and  $NO_3$  radicals) [Arey and Atkinson 2003, Estève et al 2004, Perraudin et al 2007]. Thus, chemicals primarily released into the atmosphere are transformed into degradation products (e.g., ketones and quinones, polyacids, diols, epoxides, cumulatively defined as secondary pollutants) that modify the chemical signature of the substrate as well the toxic properties of the air parcel impacted by the exhausts [Atkinson and Arey 1994, Durant et al 1999, Bandowe et al 2014]. As for airborne particulates, this reactivity introduces some uncertainty with regard to the source identification, since wide ranges of lifetime characterize organic chemicals, on the other hand, the rate of chemical degradation can be regarded as an index of air parcel ageing, i.e. of the importance of reactions developing there [Sofowote et al 2010, Cecinato et al 2014]. Instead, in the case of dusts the impact of atmospheric reactivity is by far more important, because fine particles need time to settle on surfaces and the collection period of samples usually lasts  $\geq 15$  days.

The first approaches to identify the emission sources of organic toxicants by means of molecular signatures have made in late twentieth century [Daisey et al., 1986, Harrison et al., 1996]. Focus was addressed overall to alkanes, PAHs and nitrated derivatives (NPAHs), but some investigations regarded fatty acids, halides (e.g. dioxins and furans PCDD/Fs, polychlorobiphenyls PCBs, polybromodiphenylethers PBDEs), polysaccharides (levoglucosan, mannosan), sterols (cholesterol, stigmasterol, sitosterol) and triterpenols (amyryns). Due to intrinsic limits of the simple molecular signature use, other tools have adopted preferably to trace the pollution sources impact, e.g. PCA, nevertheless, this the study of chemical fingerprints remains proper for the preliminary analysis of organic matter. Besides, molecular signature is easily integrated in statistical approaches based on a number of chemical and physical variables [Kavouras et al 2001, Mostert et al 2010, Brown and Brown 2012a/b, Khedidji et al 2017, Chen et al 2019, Maechler et al 2019, Molnar 2019, Sofowote et al 2020], which look suitable for source apportionment studies.

As for sources, interiors as a whole look as a space very different from outdoor environment. [Zhao et al 2007, Guo and Kannan 2013, Sangiorgi et al 2013, Romagnoli et al 2014, Hassanvand et al 2015, Tran et al 2015, Oliveira et al 2016, Subedi et al 2017, Liu et al 2018, Lu et al 2018, Lucattini et al 2018, Steinemann 2018, Wong et al 2019, Zhu et al 2019]. Three kinds of contaminants affect indoor locations,

i.e.: *i*) chemicals overall released outdoors and moved into the interiors through building openings and ventilation devices (e.g., hydrocarbons present in motor vehicle exhausts), *ii*) substances released indoors and outdoors at broadly analogous levels (e.g., nitrogen oxides, psychotropic substances), and *iii*) compounds predominantly released by typical indoor sources (e.g., deodorants, plasticizers). Besides, chemicals released indoors meet up environmental contours heavily different from open air, e.g., temperatures are much less varying, ozone is much less and surfaces are much larger. All of them change the chemistry of interiors, the lifetime of substances and the gas/condensed phase equilibria. Although human exposure to toxicants occurs predominantly in interiors, legislation dealing with indoor pollution is still insufficient aside of workplaces, while extensive investigations concerning the air quality of interiors deal overall with tobacco smoking.

This paper provides an overview of investigations carried out by our team, aimed at identifying the molecular fingerprints of organic fraction of airborne particulate matter and deposition dust, potentially suitable to draw information about the sources of pollution and the respective impact on the environment. Three major categories of fingerprints will be discussed, namely: *i*) individual tracers, *ii*) diagnostic concentration ratios, and *iii*) homologue percent distributions within groups.

## 2. The State-of-the-art Of Research About Molecular Signatures Of Pollution Sources

*2.1. General features of emission profiles.* Apart from environmental contour, three key factors influence the composition of emissions resulting from chemical analysis. They are: *i*) the operating conditions of emission source, including the kind of fuel, temperature of exhausts, type of abatement devices, *ii*) the procedure of collection (which includes vapors, particles or both), and *iii*) the methodology adopted to process samples and determine chemical composition. These factors make hard to assign thorough emission factors to chemicals released from the sources, and to assess precise values to concentration ratios or percentages of substances considered in the molecular fingerprints [Tobiszewski and Namiesnik 2012, Cecinato et al 2014]. Investigations undertaken with different methodological approaches can lead to not comparable results. For instance, the n-alkane profile detected in organic particulate matter depends on temperature occurring during sampling, which influences the loss rates of the most volatile compounds. Therefore, the study of n-alkanes percent distribution is mostly restricted to high molecular weight homologues, namely to hydrocarbons with carbon number  $\geq 25$  (C<sub>25</sub>). As for PAHs, compounds with similar vapor pressures and/or high molecular weights are preferred to choose the ratios of concentration to select as diagnostic of sources. Anyway, in our work the organic matter composition was determined by applying similar methodologies for all of emission exhausts, suspended particulates and dusts. The samples have first analyzed according to state-of-the-art of literature, and then chemical characterization has improved to draw further insights about the nature of sources.

*2.2. n-Alkanes.* Non-polar fraction of particulate organic matter POM includes numerous groups. They are alkanes, alkylated mono-aromatics and biphenyls, alkenes, branched and cyclic-aliphatic hydrocarbons. Among them, attention has paid overall to n-alkanes (linear homologues), alicyclic compounds have

investigated as tracers of petrol products, and methyl substituted alkanes as markers of tobacco smoking.

The saw-tooth distribution of high-molecular-weight n-alkanes has been associated to high trees [Simoneit and Mazurek 1982, Alves et al 2001, Rabhi et al 2018]. Biogenic synthesis leads to preferential generation of even C-numbered fatty acids, then, acids tend to lose CO<sub>2</sub> through the natural process of decarboxylation, and form odd-C numbered n-alkanes (or alkenes, in the case of unsaturated precursors) as final products. Since this phenomenon is more evident for long-chain homologues, the most used parameter to rate the impact of (high) vegetation is Carbon Preference Index (CPI<sub>25</sub>) [Alves et al 2001, Pio et al 2001, Omar et al 2007]. This parameter is expressed by the following formula:

$$\text{CPI}_{25} = \frac{C_{25} + C_{27} + C_{29} + C_{31} + C_{33} + C_{35}}{2 \cdot (C_{24} + C_{26} + C_{28} + C_{30} + C_{32} + C_{34})} + \frac{C_{25} + C_{27} + C_{29} + C_{31} + C_{33} + C_{35}}{2 \cdot (C_{26} + C_{28} + C_{30} + C_{32} + C_{34} + C_{36})} \quad (1)$$

where C<sub>i</sub> means the concentration of n-alkane homologue with carbon number equal to *i*.

By contrast, a mono-modal distribution with the maximum centered between C<sub>19</sub> and C<sub>26</sub> is typical of exhausts of fuels derived from petroleum, in this case, CPI<sub>25</sub> values range from 0.6 to 1.3 [Simoneit 1984, Perrone et al 2014].

For instance, we calculated CPI<sub>25</sub> equal to ~1 and exceeding 10, respectively, nearby a highway in the Algiers metropolitan area (Fig. 1A), and in a forest area of Biskra province, Algeria (Fig. 1B), instead, usually a combination of the two distributions has observed in a city garden of Rome, Italy (Fig. 1C).

Other indexes have investigated to put in evidence the impact of vegetation. They are: *i*) the homologue (C<sub>max</sub>) corresponding to the maximum concentration within the n-alkane percent distribution, and *ii*) the cumulative percentage attributable to natural waxes (NW%) [36, 63]. As for C<sub>max</sub>, motor vehicle exhausts show the prevalence of short and medium chain hydrocarbons (<C<sub>24</sub>), whilst the leaf debris of high trees is characterized by the predominance of n-C<sub>29</sub>/n-C<sub>31</sub>. The two distinct behaviors have pictured in Fig. 1A and 1B, where the maximums correspond to tricosane (C<sub>23</sub>) and nonacosane (C<sub>29</sub>), respectively.

The NW% value is provided by the formula:

$$\text{NW}\% = 100 * \frac{\sum_{12}^m C_{2n+1} - 0.5 \cdot (C_{2n+2} + C_{2n})}{\sum_{12}^m C_{2n+1}}, \quad (2)$$

Where each term at numerator is set equal to zero whereas the actual rate results <0.

Besides, carbon preference indexes analogous to CPI<sub>25</sub> have formulated considering larger n-alkane ranges (e.g., C<sub>11</sub>-C<sub>36</sub>) or the only light homologues (<C<sub>25</sub>), e.g. C<sub>15</sub>-C<sub>24</sub>. Although CPIs based on light

hydrocarbon sequences are biased due to compound volatility, these indexes allow investigating the possible impact of marine biota (algae, plankton) and microorganisms when they are combined with the presence of isoprenoids and with  $C_{max}$  corresponding to  $C_{15}/C_{17}$ , [Fisher et al 1972, Horikawa et al 2010, Wang et al 2010]. Table 1 provides a synthetic overview of what discussed above. The action of marine organism has identified also as possible source of squalene and squalane detected in offshore and coastal airborne particulates, while abietane and its homologues allowed distinguishing the coniferous emission from that of other plants and trees [Simoneit and Mazurek 1986, Fine et al 2004].

Despite the above discussed two percent distributions are the most common, n-alkanes belonging to range  $<C_{24}$  may show the prevalence of even-C homologues, this pattern has interpreted as the signature of bacteria and microorganisms [Kuhn et al 2010]. By consequence, it can occur that the whole n-alkane fingerprint exhibits high percentages of even homologues in the short/medium-chain range, and of odd homologues in the long-chain range.

The important presence of petroleum components (e.g. pristane and phytane) compared with n- $C_{17}$  and n- $C_{18}$ , respectively, has considered as a track of motor vehicle emission [Hamilton et al 1984, Alexandrino et al 2019, Alkhafaji 2021]. Though unusual, high percentages of semi-volatile homologues (from  $C_{20}$  to  $C_{26}$ ) have also detected, this pattern has found as typical of particulates contaminated with bee waxes [Guenther et al., 1995, Fine et al., 2004].

*2.3. Branched and cyclic hydrocarbons.* Complex blends of aliphatic hydrocarbons with branched and/or cyclic structure (e.g., steranes and hopanes, see Figure S1 in Supplementary Material) form the bulk of petrol industry products, like fuels and solvents, and affect the exhausts [Xiao et al 2019]. The composition profile of organic particulates shows one or two humps of “unresolved mixture” which accompany the n-alkanes sequence, the first one, comprised of light hydrocarbons, has associated with gasoline and diesel oil residues, and the second, of heavier components, to lubricating oils (see *a* and *b* humps in Fig. 2). Noteworthy, the vehicle emission profile depends on the engine working conditions, the relative importance of hump raises at unregulated driving regimens, e.g. during cold starts.

Both tobacco plant leaves and tobacco smoke fumes exhibit a particular percent profile of the non-polar organic fraction. In fact, long-chain odd *iso*-alkanes and even *anteiso*-alkanes are much richer than in other emissions [Kavouras et al., 1998]. Besides, the *normal* hentriacontane ( $nC_{31}$ ) is predominant if compared to  $nC_{29}$  and  $nC_{33}$  homologues. This molecular signature has observed in tobacco smoke chambers and in interiors heavily contaminated by smoke.

*2.4. Polycyclic aromatic hydrocarbons.* The focus of investigations on PAHs originates from the ascertained toxicity of these substances in terms of carcinogenic and mutagenic power as well as of co-promotion of hearth morbidity and premature deaths [Collins et al 1998, European Parliament and Council 2005, IARC 2012]. Since organic particulates exhibit different PAH signatures, many attempts of associating their chemical imprinting with the nature of emission have made. At this regard, it is worth to remark that the actual percentages of PAHs in emissions do not correspond to those found in PM and

dust [Kim et al 2009, Tobiszewski and Namiesnik 2012, Keyte et al 2013]. Indeed, most PAHs are released hot by organic matter burning (e.g., forest fires, fuel combustion), thus, PAHs originally exist overall as vapors, afterwards, PAHs fast condense onto carbonaceous particles dispersed in air and share their fate (e.g., settle or move across atmosphere) [Simoneit 2002, Medeiros and Simoneit 2008, Ravindra et al 2008, Lammel et al 2010]. The gas/particle equilibrium developing at the particle surface is dynamic and affected by reactivity of congeners, though the principal PAHs (e.g., the sixteen included in the list of priority pollutants [USEPA, 1993]) have classified as persistent toxicants [USEPA 1993, MacKay and Callcott 1998, Lodovici et al 2003, Cao et al 2019].

Only a handful of PAHs, both individually and as sub-groups, have associated to specific sources. Among them, the most important ones are retene (1-methyl,7-isopropylphenanthrene), dimethyl/ethylphenanthrene and benzo[ghi]fluoranthene [Tong and Karasek, 1984, Benner et al., 1995, Shen et al., 2012]. Retene is typical of wood, the second occurs as mixture of isomers labeling differently vegetation and fossil fuel combustion, and the third looks as an important component of motor vehicle exhausts. An example of that has pictured in Fig. 3, which reports the dimethyl/ethyl phenanthrene isomers MS ion trace observed in the airborne particulates of Leonessa and Rome, Italy [Petracchini et al 2017]. The GC-MS chromatogram in Fig. 3A refers to Rome downtown during the winter and mimics that of diesel exhausts. Figure 3B refers to Leonessa, a mountain town of Central Italy, the dimethyl/ethyl phenanthrenes fingerprint is analogous to that of Rome but holds some differences. Another molecular signature of dimethyl/ethyl phenanthrenes, reported in Fig. C, belonged to a second sample of Leonessa (Fig. 3C), although collected in the same year period, it was almost identical to that characterizing the wood burning. Noticeably, wood combustion is plenty exploited in that region to heat houses, cook food and dispose brushwood. The percent distribution in Fig. 3C is similar to that found in Leonessa during the summer season (Fig. 3D). For completeness of information, Figure 3E reports the GC-MS trace of retene recorded in the second winter sample of Leonessa.

Solely fresh emissions hold benzo[b]anthracene (naphthacene) and anthanthrene, known to be prone to decompose fast [Wise et al 1988, Dominguez et al 2003, Kim et al 2009]. Indeed, the occurrence of these compounds has documented in exhausts but has not regularly in the atmosphere.

Due to contemporary occurrence of a number of PAHs, the usual approach aiming at drawing insights about the nature of emissions considers the concentration ratios of individual substances [Ravindra et al 2008, Katsoyiannis et al 2011, Katsoyiannis and Breivik 2014]. The most common concentration PAH ratios used to identify the sources are fluoranthene vs. pyrene (FA/PY). benz[a]anthracene vs. chrysene (BaA/CH), indeno[1.2.3-cd]pyrene vs. benzo[ghi]perylene (IP/BPE), and benzo[a]pyrene vs. benzo[ghi]perylene (BaP/BPE). Other ratios, e.g. phenanthrene vs. anthracene (PHE/AN), total methylphenanthrene vs. phenanthrene (SMPHE/PHE) and unsubstituted PAHs vs. total PAHs including alkyl-substituted congeners (parent-PAHs/ SPAHs) are investigated less frequently. Table 2 provides a list of PAH diagnostic ratios and the respective values calculated for several categories of emissions, as described by scientific literature. The lack of unequivocal digits labeling the type of emission leads the Authors to consider small intervals of values for each PAH concentration ratio, and groups of three or four

pairs of compounds. The benzo[a]pyrene/benzo[e]pyrene ratio (BaP/BeP) merits a separate discussion. Indeed, for a long time BeP has not been investigated, because it was considered poorly carcinogenic with respect to other PAHs. On the other hand, it occurs in emissions at similar extents as benzo[a]pyrene, but is more persistent. Thus, the concentration ratio of the two isomers is close to 1.0 in fresh exhausts but tends to drop, overall in the presence of oxidants. For instance, in a monitoring campaign carried out in Milan, Italy, during 1991, we found BaP/BeP concentration ratios  $\sim 0.9$  in February and March, and  $\sim 0.1$  in September, although the sampling location was unchanged and the site was under a quite constant source, namely heavy traffic (Cecinato 1997). Whereas used alone, the information obtained through molecular signatures looks insufficient to quantify the contribution of each source to pollution, however, it helps to recognize the principal sources. Besides, to put in the evidence the degradation of primary emissions begins important when the toxicity of final products (e.g., PAH quinones and lactones) exceeds that of the parent compounds [Durant et al 1999].

*2.5. Nitrated polycyclic aromatic hydrocarbons (NPAHs).* NPAHs gained concern when it was demonstrated that emissions contain many chemical belonging to this group [Hoekman 1992, Zielinska et al 2004, Liu et al 2010]. These investigations based its *raison d'être* in the huge increment of diesel engine vehicles during '70s and '80s of the last century, promoted by tax benefits. In fact, diesel engines have been recognized as major sources of NPAHs, capable of giving reason for the NPAH occurrence in the atmosphere [Bamford and Baker 2003, Bandowe et al 2014, Bandowe and Meusel 2017]. On the other hand, many NPAHs have been ascertained as direct mutagens and cancer promoters [Gbeddy et al 2020]. Attention has been paid overall to a list of NPAHs whose contribution to toxicity of air particulates has even been estimated, they are nitrated derivatives of naphthalene, fluorene, anthracene, fluoranthene, pyrene, benz[a]anthracene and chrysene.

However,  $\text{NO}_2$ -position isomers associated to PM do not correspond to those mainly affecting emissions. In particular, 2-nitrofluoranthene and 2-nitropyrene are commonly absent in exhausts, but exist as products of in-situ reactions developing in the atmosphere (see Figure 4A/B) and sometimes are the most abundant NPAH affecting airborne particulates [Bamford and Baker 2003, Bandowe and Meusel 2017].

The molecular signature nitrofluoranthenes and nitropyrenes has been used to parameterize the relative importance of direct emission and action of oxidants. Taking in account the nitration rate of precursors reacting with OH radicals and  $\text{NO}_2$ , it has been suggested that photochemical reactivity is more important than vs. direct emission when the 2-NFA/1-NPY ratio exceeds the value of 5 [Pitts et al, 1985]. Instead, the formation of 4-NPY is feasible only in the presence of  $\text{NO}_3$  or  $\text{N}_2\text{O}_5$  which develop after sunset through reaction of  $\text{O}_3$  and  $\text{NO}_2$ .

*2.6. Fatty acids and alcohols, polar compounds.* Medium and long-chain acids exist overall as released by living organisms [Goutx and Saliot 1980, Kawamura and Gagosian 1987, Lindbeck and Puxbaum 1999, Oliveira et al 2007, Bi et al 2008, Sangiorgi et al 2013, Balducci et al 2014]. The percent distribution pattern of fatty acids reveals the clear prevalence of even carbon atom homologues, and the rates of carbon preference indexes (ACPIs), formulated similarly to those of n-alkanes, can exceed the rate of ten

[Alves and Pio, 2001]. Other sources show analogous profiles, e.g., vehicle exhausts hold  $A_{12}$ - $A_{22}$  acids (i.e., linear chain homologues with 12÷22 carbon atoms), with the maximums corresponding to  $A_{16}$  and  $A_{18}$ . Biogenic emissions show also typical percentages of medium- and long-chain fatty acids. Usually, apart from palmitic ( $A_{16}$ ) and stearic ( $A_{18}$ ) acids, the profiles have a secondary maximum within the ranges  $A_{20}$ ÷ $A_{24}$ , or  $>A_{25}$ , light homologues have associated with microbiota, small plants, softwood trees, while heavy acids characterize high plants and hardwood trees [Gelpi et al., 1970]. Besides, in the case of microorganisms the ACPI rates are lower, due to important percentages of odd-carbon acids from  $A_{15}$  to  $A_{21}$ .

Unsaturated and dicarboxylic acids merit a special mention. Unsaturated acids ( $UA_n$ ), e.g. palmitoleic ( $UA_{16}$ ), oleic ( $UA_{18}$ ) and linoleic (twin unsaturated  $A_{18}$ ), are indicative of emission from crops. Dicarboxylic fatty acids ( $DA_n$ ) exist as minor components released by vegetation, whose emissions show the usual even-to-odd carbon prevalence, however particulate matters are rich of  $D_2$ - $D_6$  homologues, due to contribution of anthropogenic sources. Nevertheless, reacted air parcels reveal the important occurrence of azelaic acid ( $DA_9$ ), which is a by-product of oleic acid decomposition [Balducci et al 2014, Kawamura and Bikkina 2016, Ren et al 2020].

Linear alcohols, 2-ketones, aldehydes, fatty acid methyl esters and nitriles have not extensively investigated as source tracers of suspended particulates, though all of them have linked to emission from vegetation [Simoneit and Mazurek 1982, Simoneit 2002] and have found in pyrolysis by-products of sewage sludge treated with aerobic and anaerobic digestion [Dominguez et al 2003]. Linear alcohols exhibit a behavior parallel to fatty acids. They display the predominance of even carbon homologues and are among the principal components of organic particulates in rural regions [Simoneit and Mazurek 1982]. Many sterols also (e.g., sitosterol, stigmasterol and amyryns) have associated to vegetation as components of epicuticular waxes. The most important exception is cholesterol, which has recognized as a tracer of meat cooking [Cass 1998, Carreira et al 2009]. Other acid esters (including biopolymers) are employed nowadays as alkyl phthalate surrogates, because these latter have classified as emerging contaminants [Cavanah et al 2018, Udayakumar et al 2021]. Thus, the occurrence of new esters in soot and dust is indicative of contamination by plastics.

A set of polar organics, including nicotine and its derivatives, e.g. cotinine and nitrosamines, have proposed as tracers of mainstream, sidestream and third-hand tobacco smoke [Hecht 1999, Hammond et al 1987, Daisey 1999, Apelberg et al 2013, Blanchard et al 2014], nevertheless, quantitative estimates of impact on the environment have attempted only by means of nicotelline [Aquilina et al 2021].

*2.7. Organic halides.* Polychlorobiphenyls (PCBs) and polychlorinated dioxins and furans (PCDD/Fs) are probably the most investigated groups of halides affecting the environment [Barbas et al 2018]. PCBs were important industrial products, because they had a number of applications as mixtures (power transformers, heat exchangers, substrates for pesticides and inks, solvents), by contrast, PCDDs and PCDFs exist solely as unwanted by-products of other industrial processes (e.g., paint manufacturing,

foundries and steel mill). Despite PCBs and PCDD/Fs have banned since long time, both groups still affect the environment [Ngo et al 2020]. Industrial syntheses of PCBs lead to blends characterized by various average chlorine percentages, which sometimes could aid in highlighting the impact of sources suspected to cause environmental pollution. Various fingerprints label the emission sources, for instance, distinct PCDD/Fs patterns have observed for vehicle exhausts and steel mill fumes [Liu et al 2015]. Besides that, the molecular fingerprints of PCBs and PCDD/Fs change with time owing to ability of congeners to persist to degradation as well as to dissolve in waters and lipids [Di Guardo et al 2017, Ngo et al 2018, Ngo et al 2020]. Finally, it is very important to take in account the not negligible volatility of organic halides. For instance, 2,3,7,8-tetrachlorodibenzo-p-dioxin occurs overall as vapor in the environment, whilst dioxin-like congeners are adsorbed on particulates [Barbas et al 2018], owing to their key role in toxicity, the contemporary collection of gaseous and condensed phases of atmosphere and emissions is mandatory to draw information about sources and air quality.

Other halides have recently gained importance, as tracers of water, air and soil pollution caused by waste spill and contaminated food. In particular, polybromodiphenyl ethers (PBDEs) and organic esters of phosphoric acid are present in flame retardant formulas [Lee et al 2020, Percy et al 2020], while perfluoroalkyl acids (PFAs) and other perfluorinated chemicals enjoy of many industrial and home care applications as surfactants [Hubbard et al 2012].

*2.8. Polysaccharides.* The occurrence of numerous organic substances in the environment has recognized as linked with biomass burning in general, and specifically to that of specific tree species [Oros and Simoneit 2001a/b, Oros et al 2002]. Many are the by-products of lignine (e.g., methoxyphenols) [Hawthorne et al 1988, Hays et al 2005], as well as those emerging from dehydration-polymerization of carbohydrate molecules (levoglucosan, galactosan, mannosan, inositols). Levoglucosan in particular, typical tracer of wood burning, allowed to demonstrate that even big city downtowns undergo the impact of this kind of emission, due to the generalized use of wood for heating and cooking [Fine et al., 2004] in the countryside. Indeed, wide uncertainty remains associated to the emission rate of these chemicals, nevertheless, according to levoglucosan levels in air, manmade biomass burning looks as the principal source of pollution outside of cities and heavy industry districts [Pomata et al 2014, Perrino et al 2019, Ren et al 2020].

### **3. Materials And Methods**

To improve the knowledge of molecular signature of particulate organic matters, we investigated the chemical composition of groups of samples collected in Italy and abroad. The samples were collected from air both indoors and outdoors (airborne particulates and settled dusts). All of them have analyzed in the frame of cooperative research programs with Regional Agencies for Air Pollution Control, Italy, Universities of Algiers (USTHB) and Ouargla, Algeria, Technopolis of Borj Cedria, Tunisia, Ministry of the Environment (MATTM), Italy, as well as proprietary CNR-IIA projects.

The sampling procedures and the analytical methods adopted to characterize the composition of targeted particulates are described elsewhere [Ciccioli et al 1989, Yassaa et al 2001, Mabilia et al 2004, Mininni et al 2004, Paolini et al 2015, Rabhi et al 2018]. Sampling procedures in compliance with European normative for PM<sub>10</sub> have applied. They consisted of active aspiration of air at 2.32 m<sup>3</sup>/h flow rate and filtration through inert membranes in Teflon. Settled dust has collected from free surfaces according to the method optimized in our institute [Cecinato et al 2014, Romagnoli et al 2014]; ultra-pure aluminum foils or cotton swabs have stretched out over pre-cleaned surfaces at 1.5 ÷ 2.0 m above ground and exposed 15 days. To minimize changes in chemical composition, the samples have individually sealed in plastic boxes and stored in a freezer until analysis.

Procedures adopted to solve chemical composition of samples comprised: *i*) extraction with organic solvent; *ii*) fractionation; and *iii*) instrumental analysis through gas chromatography – mass spectrometry (GC-MS) [Cecinato et al 2014, Romagnoli et al 2014, Mabilia et al 2004, Paolini et al 2015]. Organic fraction has recovered from the substrate through extraction in ultrasonic bath, using a dichloromethane/acetone mixture. After reduction close to dryness, the extracts have fractionated through chromatography on neutral alumina or silica gel column; three classes of polarity have separated through eluting the column with isooctane, isooctane/dichloromethane and dichloromethane/acetone, in sequence. Instrumental analysis was performed by applying GC-MS methods based on (DB5-MS type) capillary column separation, electron-impact ionization of analyte molecules and total ion current (TIC) or selected-ion (SIM) recording. Injection has operated in split-less mode, chromatographic runs has conducted in gradient of temperature up to 290°C, and peak recognition achieved by means of characteristic molecule and fragment ion current signals, coupled with peak retention times. The internal standard method, based on the use of perdeuterated homologues as reference of native compounds, has adopted for quantitative purposes.

## 4. Results And Discussion

Until now, scarce attention has paid to unsaturated hydrocarbons. Nevertheless, in the light range of non-polar fraction of POM (corresponding to hydrocarbons with 12 up to 20 carbon atoms in the molecule, namely C<sub>12</sub>÷C<sub>20</sub>) we could distinguish three distinct fingerprints. They were: *i*) the predominant occurrence of n-alkanes (n-alkenes negligible); *ii*) the prevalence of n-alkenes (with high dodecene/dodecane and tetradecene/tetradecane ratios, and low octadecene/octadecane and eicosene/eicosane ratios); and *iii*) a mixed behavior. The three fingerprints have shown in Figure 5. Sample A (dust collected indoors at El Bey, Tunisia, held much more n-alkanes than alkenes (Fig. 5A1/A2); dusts from Tipaza, Algeria (Fig. 5B1/B2) included both alkanes and alkenes; n-alkene concentrations exceeded those of n-alkanes in dusts of Reggio Calabria, Italy (Fig. 5C1/C2).

At our knowledge, no exhaustive explanation of the three distinct patterns has provided. Even n-alkene homologues presumably are directly released by unknown sources or originate from the twofold decarboxylation of unsaturated even *a,w*-diacids, but further investigations are needed to link these fingerprints with anthropogenic and biogenic emissions.

As for tobacco smoking, both in airborne particulate and dust collected at a frequent smoker's home in Rome, Italy, *anteiso* C<sub>30</sub>, C<sub>32</sub> and C<sub>34</sub> alkanes were more abundant than the respective *normal* homologues. Besides, the concentration of *normal* C<sub>31</sub> exceeded the average of nC<sub>29</sub> and nC<sub>33</sub>. Both molecular signatures are similar to those found in smoke chambers (Figure 6).

According to that, we have tried to pinpoint two new quantities to index the impact of tobacco smoking on the environment. They are average tobacco smoke ratio (ATSR) and average anteiso/iso concentration ratio (AICR), defined by the following formulas:

$$\text{ATSR} = (iC_{29}/nC_{29} + aC_{30}/nC_{30} + iC_{31}/nC_{31} + aC_{32}/nC_{32} + iC_{33}/nC_{33} + aC_{34}/nC_{34})/6 \quad (3)$$

$$\text{AICR} = (aC_{29}/iC_{29} + aC_{30}/iC_{30} + aC_{31}/iC_{31} + aC_{32}/iC_{32} + aC_{33}/iC_{33} + aC_{34}/iC_{34})/6 \quad (4),$$

where  $iC_j$ ,  $aC_j$  and  $nC_j$  indicate iso-, anteiso- and linear alkanes with  $j$  carbon atoms in the molecule.

Instead of identifying one only ratio among the anteiso/iso/normal alkane sequence, we computed all concentration ratios of ATSR and AICR formulas over the C<sub>29</sub>-C<sub>34</sub> range in order to reduce uncertainty associated to small changes in emission profiles of other possible sources. To assess the correctness of this approach, both ATSR and AICR rates have evaluated in airborne particulates and dusts collected both at urban and rural sites. The results have shown in Table 3.

ATSR values ranged from 0.05 to 1.30, with the minimums corresponding to rural sites and the maximums found in locations heavily affected by tobacco smoke. ATSR and AICR values calculated in the case of outdoor samples put in the evidence the impact of tobacco smoking, which was in agreement with the ubiquitous occurrence of nicotine in the city air [Rabhi et al 2018 and references herein]. In general, dusts showed ATSR and AICR values lower than airborne particulates; that is in accordance with the nature of dust, which includes coarse grains of various origin, whilst tobacco smoke is comprised of fine and ultra-fine particles accounting for only a fraction of total particulate mass. Noticeably, ATSR and AICR values in the dust and at the balcony of smoker house (see the sixth column of Table 3) were quite high, confirming the importance of tobacco smoke in interiors and even at open air. Though still insufficient to draw semi-quantitative information about the contribution of tobacco smoke to environmental pollution, the molecular signature of long-chain alkanes, seems more attractive than nicotine and its derivatives, which are more volatile and degradable. Presumably, it can suitably combine with the monitoring of nicotelline.

## Conclusion

Molecular signature of organic contaminants affecting airborne particulates and dusts comprise individual markers and, more often, distribution patterns within the homologue groups. Both tools provide preliminary but suitable information about nature of emissions and with regard to their health impact on environment. Further investigations are necessary to elucidate the sources of chemical fingerprints newly observed. In particular, the progress in knowledge of molecular fingerprints will help investigators in

applying more sophisticated approaches (e.g., principal component analysis, source factorization modelling) to assess the relative importance of emissions. That will help to optimize the strategies aimed at controlling air pollution and mitigating the toxicants impact on humans and environment.

## Declarations

**Author Contributions.** This paper originates from specific contributions of the Authors. They are:

*Dr. Angelo Cecinato* ([angelo.cecinato@uniroma1.it](mailto:angelo.cecinato@uniroma1.it); [angelo.cecinato@iia.cnr.it](mailto:angelo.cecinato@iia.cnr.it)): result analysis, conceptualization of molecular signature indexing, original and revised draft preparation, writing and editing;

*Prof. Alessandro Bacaloni* ([alessandro.bacaloni@uniroma1.it](mailto:alessandro.bacaloni@uniroma1.it)): supervision and training of doctorate thesis work;

*Dr. Paola Romagnoli* ([romagnoli@iia.cnr.it](mailto:romagnoli@iia.cnr.it)): chemical analysis of dust and suspended particulate samples;

*Tech. Mattia Perilli* ([perilli@iia.cnr.it](mailto:perilli@iia.cnr.it)): in-field campaign preparation, performance and management; paper reviewing;

*Dr. Catia Balducci* ([balducci@iia.cnr.it](mailto:balducci@iia.cnr.it)): chemical procedure setup; sample analysis; investigation performance and management; writing (reviewing, revised manuscript editing).

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**Ethical Approval and Consent to Participate:** This study did not involve experiments on humans or animals. It consisted of analysis of literature regarding chemical composition of tobacco smoke, as well as of data series about organic matter associated to airborne particulates and dusts, set up in the frame of research programs performed by the Authors.

**Institutional Review Board Statement.** Not applicable: This study did not involve tests on humans or animals.

**Informed Consent Statement.** Not applicable (no experiments have made on humans or animals).

**Consent to Publish:** All Authors agreed on submitting the manuscript, to publish it in ESPR Journal Editorial Board.

**Consent for Publication:** Not applicable. The manuscript does not contain any individual person's data, since none was subject of investigation nor personal data treatment.

**Data availability.** The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request. Anyway, those not directly produced by personal

investigations of Authors are available in the bibliography cited in the paper.

**Conflicts of Interest.** The authors declare they are not under any conflict of interest condition.

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## Tables

**Table 1.** Indexes describing the n-alkane percent distributions, typical of various emission types.

index / source	petroleum	algae	microorganisms	high trees	vegetation	anthropogenic
C <sub>max</sub>	C <sub>16</sub> ~C <sub>21</sub>	C <sub>17</sub> , C <sub>19</sub> , C <sub>21</sub> , C <sub>23</sub>	C <sub>16</sub> , C <sub>18</sub> , C <sub>20</sub>	C <sub>29</sub> , C <sub>31</sub> , C <sub>33</sub>	C <sub>25</sub> , C <sub>27</sub> , C <sub>29</sub>	C <sub>16</sub> ~C <sub>23</sub>
CPI <sub>25</sub>	0.7-1.3		>1	>10	>3	0.8-1.3
CPI <sub>11</sub>	0.8-1.2	> 1.0	< 1.0			
NW%	~0			>75	>75	~0-30

*Symbols: ATSR = tobacco smoking index [see formula (3) in the text]; AICR = mean of anteiso/iso-alkane concentrations [see formula (4) in the text]; SH = tobacco smoker house; NSH = no tobacco smoker house.*

**Table 2.** Rates of the principal PAH concentration ratios currently used as diagnostic tools to draw insights about the nature of source. References: Kavouras et al 2001, Tobiszewski and Namiesnik 2012, Cecinato et al 2014).

source	type	FA/PY	BaA/CH	IP/BPE	BaP/BPE	BaP/BeP
vehicles	mixed	0.60			0.55	
	gasoline	0.54	0.8-1.3	0.20-0.35	0.35	0.95
	diesel	0.8-1.1	0.38	0.65-1.1	0.8-1.1	0.50
domestic heating	coal		0.65	0.9-1.3	1.57	
	wood, pine	0.78	0.64	1.1-1.6	1.94	2.1
	wood, oak	0.75	0.70	1.2-1.6	1.77	1.77
	synthesis fuel	1.19	0.78	1.1	1.91	
	heavy oil	0.83	1.01	1.6	0.81	0.52
steel plant	coke		0.65	0.9-1.3	1.57	
	power (coke)	0.66	0.56	2.0	0.88	2.57
tobacco smoke	particulate	0.96	1.3	0.18	0.23	0.38
waste fumes	landfill	1.3	0.84	0.76	0.70	0.55
	incinerator	≈17	0.71	0.92	~0.12	0.01

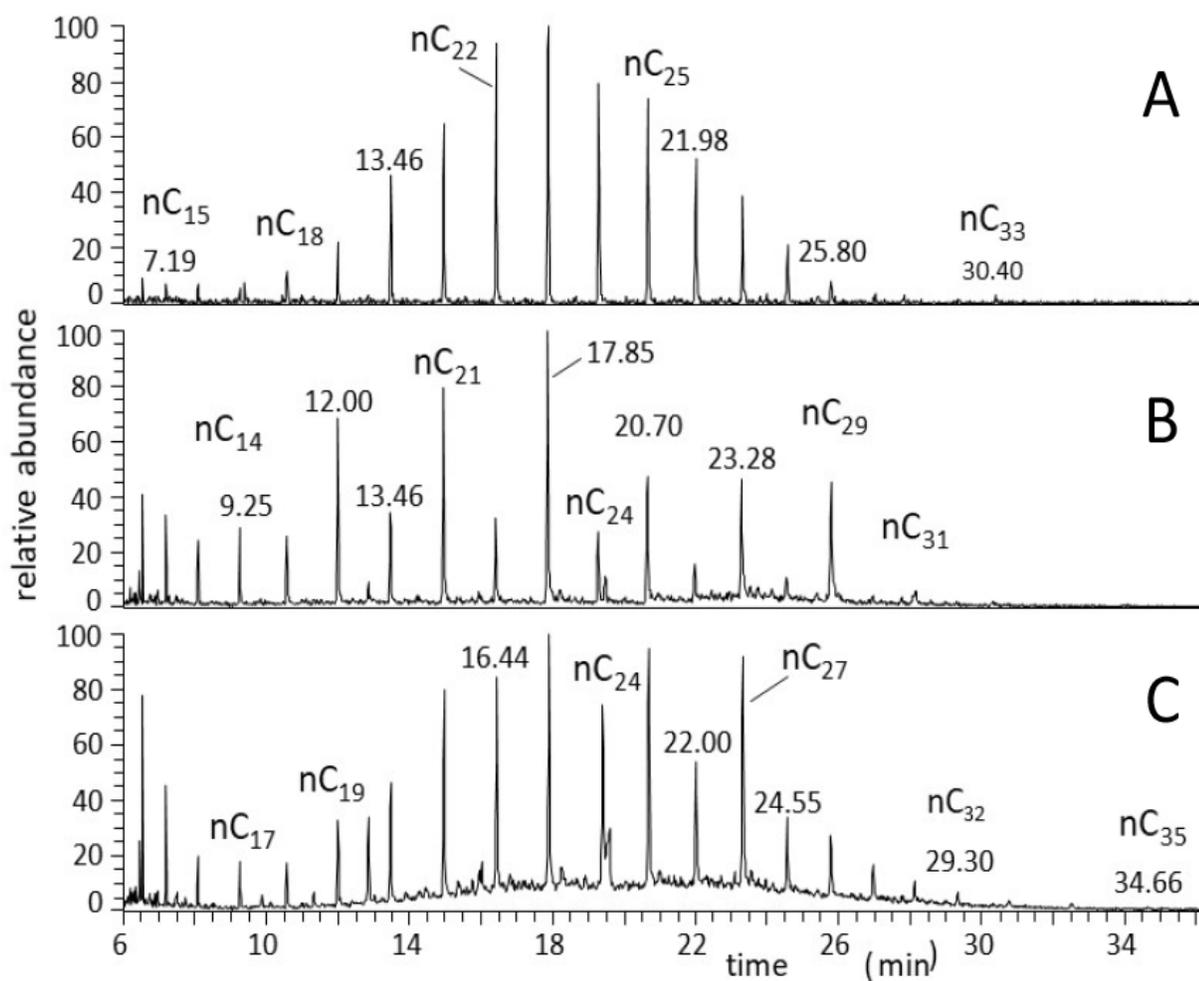
**Table 3.** ATSR and AICR index rates of airborne particulates (PM) and settled dust collected in Algeria and Italy. The number of locations investigated in each group has reported between parentheses. Site types: Lazio, urban and rural; Italy and Algeria, urban. Symbols: SH = frequent smoker home, NSH = no smoker home.

PM, outdoor	sites	Lazio region	Italy	Italy	SH, Italy	Algeria
	year time	summer (10)	summer (10)	winter (10)	spring (8)	summer (4)
	ATSR	$0.11 \pm 0.05$	$0.24 \pm 0.07$	$0.24 \pm 0.08$	$0.54 \pm 0.12$	$0.12 \pm 0.02$
	AICR	$1.50 \pm 0.46$	$1.54 \pm 0.28$	$1.70 \pm 0.35$	$3.56 \pm 0.50$	$1.35 \pm 0.15$
PM, indoor	sites	SH, Italy	SH, Italy	school, Italy		
	year time	spring (19)	winter (16)	winter (16)		
	ATSR	$1.16 \pm 0.05$	$1.15 \pm 0.00$	$0.30 \pm 0.04$		
	AICR	$5.22 \pm 0.08$	$4.48 \pm 0.20$	$1.85 \pm 0.25$		
dust, indoor	sites	SH, Italy	NSH, Italy			
	year time	spring (19)	summer (14)			
	ATSR	$0.27 \pm 0.09$	$0.10 \pm 0.03$			
	AICR	$2.00 \pm 0.95$	$1.08 \pm 0.10$			

## Supplementary

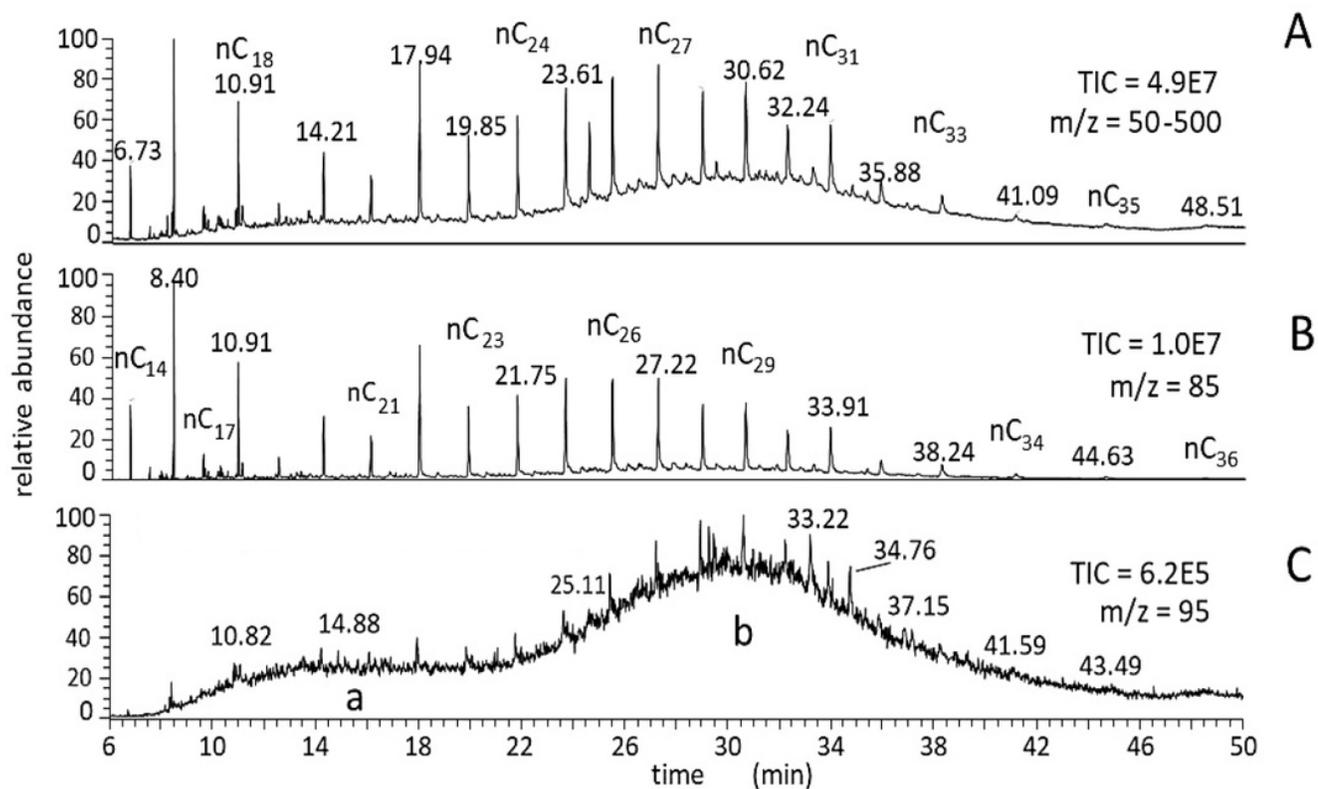
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## Figures



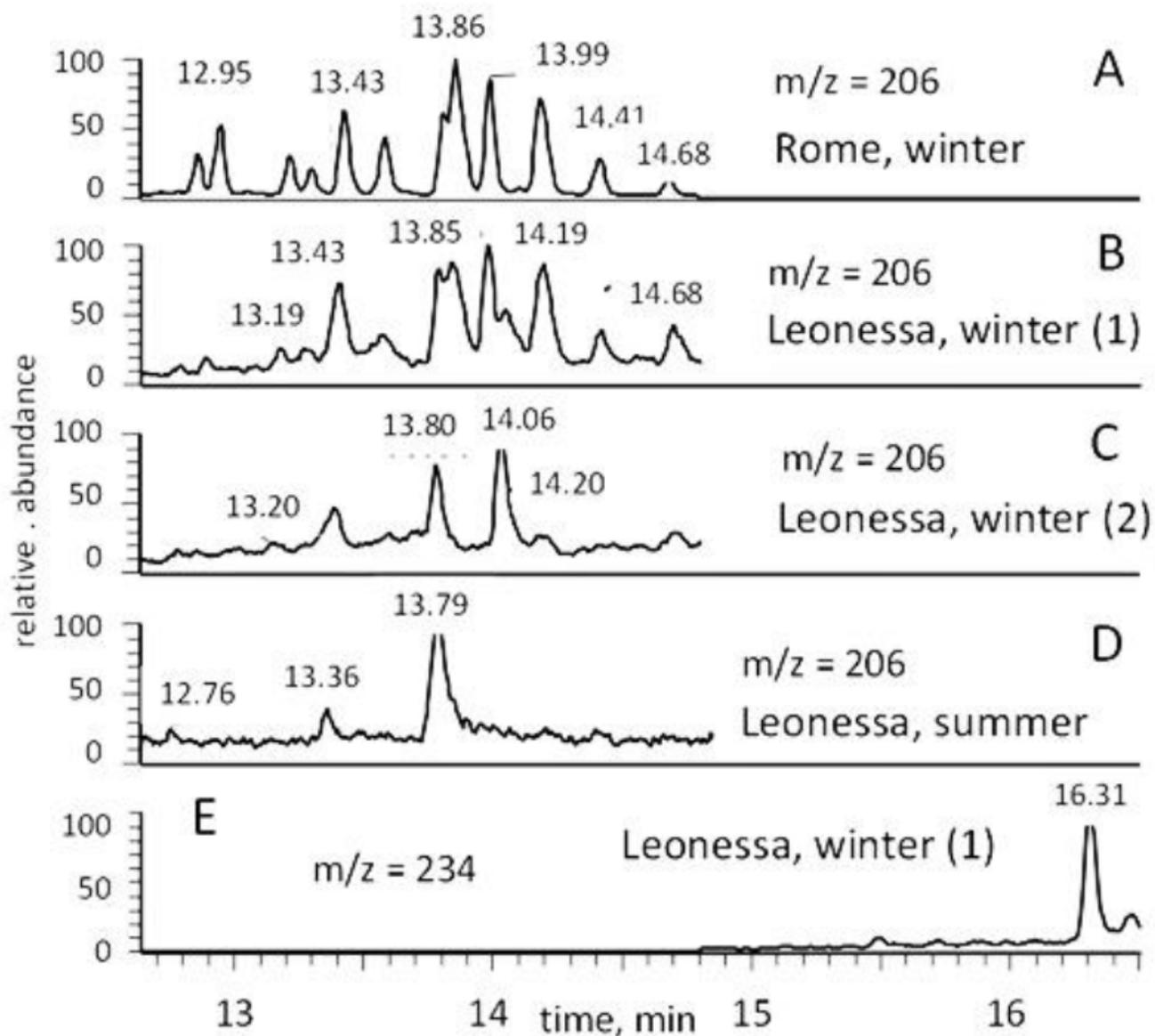
**Figure 1**

GC-MS profiles of the non-polar fraction ( $m/z = 85$ ) of airborne particulates collected at four sites variously influenced by emission sources. A) road traffic site; B) rural region; C) urban location (city garden). Symbols: nC<sub>i</sub> indicates the n-alkane with carbon number equal to i.



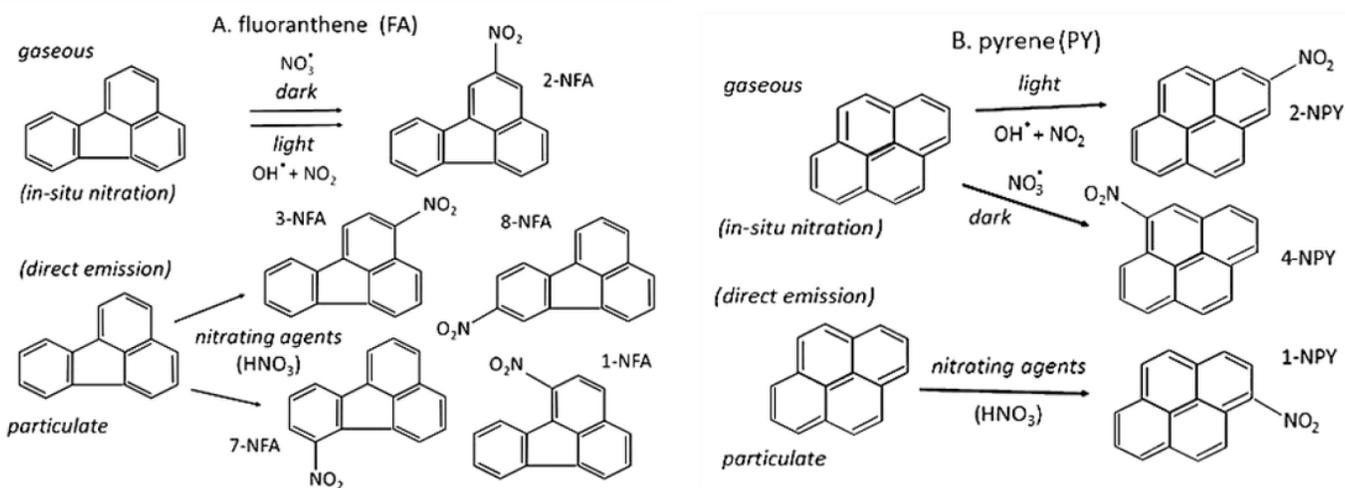
**Figure 2**

GC-MS profile of the non-polar fraction of diesel exhaust. A) total ion current signal; B) ion trace corresponding to  $m/z = 85$  (labeling n-alkanes); C)  $m/z = 95$  ion trace (branched alkanes). Both a and b humps occur in the UCM. Symbols: nCi indicates the n-alkane with carbon number equal to i.



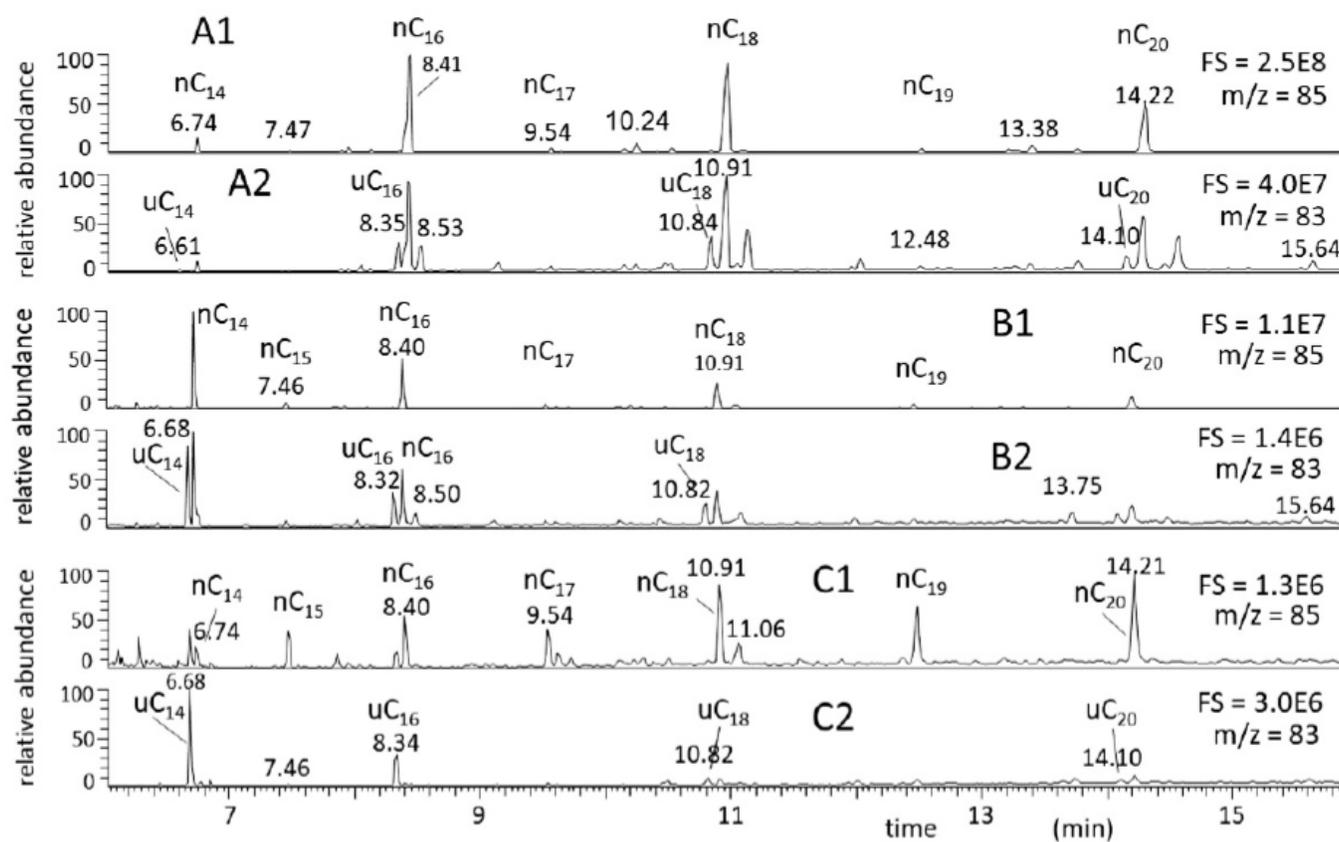
**Figure 3**

GC-MSD profiles of PAH compounds affecting the suspended particulates of Rome and Leonessa, Italy. A) Dimethyl/ethyl phenanthrenes in Rome downtown, winter season; B) Dimethyl/ethyl phenanthrenes in Leonessa, winter (sample 1); C) Dimethyl/ethyl phenanthrenes in Leonessa, winter (sample 2); D) Dimethyl/ethyl phenanthrenes in Leonessa, summer season; E) Retene in Leonessa, winter (sample 2).



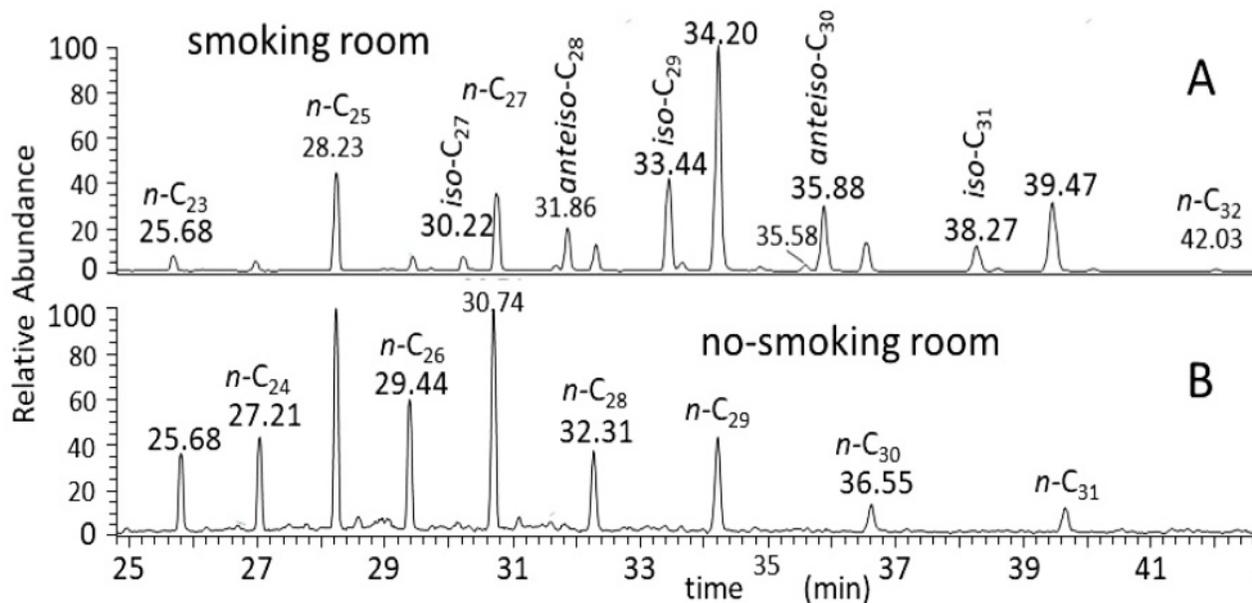
**Figure 4**

Ways of fluoranthene and pyrene nitration leading to formation of distinct nitro-substituted isomers affecting the atmosphere. A) fluoranthene; B) pyrene



**Figure 5**

GC-MS chromatograms of airborne particulate extracts. A1) El Bey, Tunisia,  $m/z = 85$  (n-alkanes); A2) El Bey, Tunisia,  $m/z = 83$  (n-alkenes); B1) Tipaza, Algeria,  $m/z = 85$  (n-alkanes); B2) Tipaza, Algeria,  $m/z = 83$  (n-alkenes); C1) Reggio Calabria, Italy,  $m/z = 85$  (n-alkanes); C2) Reggio Calabria, Italy,  $m/z = 83$  (n-alkenes).



**Figure 6**

GC-MS profiles ( $m/z = 85$ ) of dusts collected in interiors. A) private house, frequent smoker dwelling; B) waiting room, public hospital.