Indicators of Natural and Anthropogenic Emission Source Impact

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Research Article

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Abstract: The composition of organic fraction released in emissions varies with its nature and contour conditions; hence, the chemical signature of atmospheric particulate matter and dusts are investigated to identify the pollution sources and assess the respective aftermaths on environment and health. For this purpose, three complementary tools are usually adopted, i.e. specific source markers, concentration ratios of pairs of congeners, and percent distribution profiles of homologues (including derived "carbon preference indexes"). This paper provides an overview of investigations dealing with chemical signature of emission sources, applied to non-polar aliphatic (alkanes), aromatic (PAHs, Nitro-PAHs) and polar (fatty acids, organic halides, polysaccharides) organics affecting atmospheric particulate matter and deposition dust. Despite a rich literature is nowadays available, further investigations seem necessary to clarify the nature, sources and behaviors of mid-volatile, non-polar organic contaminants. More sophisticated investigations have gained importance recently (principal component analysis, source factorization modelling), nevertheless molecular fingerprints remain suitable to draw primary insights about the nature and impact of sources of environmental pollution.

Introduction

Whenever pollution rouses acute or chronic harmful effects on humans and/or injures the environment, the knowledge of nature, rate and land spread of emissions results crucial in the perspective of mitigating the impact of toxicants [Albaiges et al 1984, Bascom et al 1996, Yassaa at al 2001, Ma et al 2015, Błaszczyk et al 2017, Sifakis et al 2017, Cetin et al 2018, Nieder et al 2018, Vaz 2018]. Hence, chemical and physical characterization of gas and particulate phases plays a primary role not only to picture the outcome of release of pollutants (i.e., evaluating concentrations of selected chemicals instantaneously or averaged over suitable times and comparing them with legislative requirements), but also to assess the relative importance of sources affecting the target site or land [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, e.g. fine fraction, and grains deposited on surfaces and soil as dust) look as an important tool of investigation and at the same time a challenge, due to their complexity and variety. Organics are classified in a number of groups, which display very different properties like acidity/alkalinity/neutrality, grade of polarity, water and n-octanol solubility, vapor pressure, inertness vs. oxidants and light: linear and cyclic alkyl compounds, polycyclic aromatic hydrocarbons, acids, amines (both aliphatic and aromatic),

carbonyls, halides, organic sulfates and phosphates, etc.. Many of them are primarily associated to specific biogenic and anthropogenic sources; hence, they have been identified as tracers of living organisms, natural phenomena and man's activities.

Unfortunately, only in a handful of happy cases one substance is unequivocally and peculiarly typical of one emission, so that it allows highlighting and even estimating the impact of the source. Rather, many chemicals are released by many sources, hence the distribution models among and within the organic groups can help. For instance, biofuels are usually richer of esters than fossil fuels, and the reverse occurs for polycyclic aromatic hydrocarbons (PAHs) [Damanik et al 2018]. Again, the percentages of PAHs associated to ultra-fine, fine and coarse fractions of suspended particulate change with the emitter features [Zielinska et al 2004]. Finally, chemicals directly released in exhausts (primary emissions) undergo the 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], giving rise to degradation products (e.g., ketones and quinones, polyacids, diols, epoxides: secondary pollutants) that modify the chemical signature of the substrate as well toxic properties of the air parcel [Atkinson and Arey 1994, Durant et al 1999, Bandowe et al 2014]. For airborne particulates, this reactivity introduces some uncertainty about source recognition due to different lifetimes characterizing the compounds; on the other hand, the rate of changes is an index of air parcel ageing, i.e. of the importance of reactions developing there [Sofowote et al 2010, Cecinato et al 2014]. By contrast, dusts necessarily hold the impact of atmospheric reactivity, because collection times usually cover ≥15 days.

Historically, the molecular signature approach to identify the emission sources of organic toxicants started in late twentieth century and encountered changing appreciation along the decades [Daisey et al., 1986; Harrison et al., 1996]. Focus was addressed overall to alkanes, PAHs and nitrated derivatives (NPAHs), but investigations have also interested fatty acids, halides (e.g. dioxins and furans PCDD/Fs, polychlorobiphenyls PCBs, polybromodiphenylethers PBDEs), polysaccharides (levoglucosan, mannosan), sterols (cholesterol, stigmasterol, sitosterol) and triterpenols (amyrins). Recently, more sophisticated statistic approaches (e.g., PCA) nowadays trendy do not substitute the traditional look to molecular signature but integrate it in a more comprehensive approach computing 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].

In this context, interiors look as another world [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]. Although human exposure to toxicants it much longer indoors, legislation dealing with indoor pollution is still insufficient. Three kinds of contaminants are ascertained affecting indoor locations, i.e.: *i)* chemicals overall released outdoors, and entering the interiors through building openings and ventilation devices (e.g., traffic related hydrocarbons); *ii)* substances released indoors and outdoors at broadly analogous levels (e.g., nitrogen oxides, psychotropic substances); and *iii)* compounds predominantly released indoors by typical sources (e.g., deodorants, plasticizers). Nevertheless, so far the nature of sources and the respective importance with regard to air quality of interiors has been poorly investigated except for tobacco smoking.

This paper provides an overview of investigations carried out by our team, concerning the organic fingerprints use for source recognition/apportionment of particulates. Three major categories of fingerprints will discussed, namely: *i)* individual tracers; *ii)* diagnostic concentration ratios; and *iii)* homologue percent distributions within groups.

Materials and Methods

The sampling procedures and the analytical methods adopted by our team to characterize the composition of emissions and airborne 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 were based on active aspiration from effluents or air, respectively, for emissions and aerosols, while dust was collected from free surfaces according to method foreseen for depositions [Cecinato et al 2014, Romagnoli et al 2014].

Chemical analyses comprised solvent extraction with organic solvents (in soxhlet or ultrasonic bath), extract fractionation/clean up through column chromatography, and gas chromatography – mass spectrometric characterization [Cecinato et al 2014, Romagnoli et al 2014, Mabilia et al 2004, Paolini et al 2015].

Results and Discussion

General features of emission profiles. Apart from environmental contour, three key factors regulate the chemical composition of emissions. They are: *i)* the operating conditions of emitter, including the kind of fuel, fume temperature, type of abatement devices; *ii)* procedure of collection (vapors and particles); and *iii)* methodology adopted to process samples and chemically characterize them. These factors make questionable assigning precise emission factors of chemicals from sources, as well as assessing unequivocal rates of concentration ratios or percentages to substances [Tobiszewski and Namiesnik 2012, Cecinato et al 2014]. Analogously, the comparison of outcomes from investigations resorting to different instrumental approaches (e.g., PAH concentration ratios drawn using different analytical techniques) looks somehow biased. For instance, when considering the n-alkane profile, ambient temperature during collection and analytical procedure adopted influence the loss rates of the most volatile homologues. Hence, the analysis of distribution model of the group is often restricted to homologues with carbon number ≥ 25 (n-C_{25}). Analogously, in the case of PAHs the concentration rates of congeners with the same molecular weight are preferably considered, e.g., pyrene vs. fluoranthene; indeno[1.2.3-cd]pyrene vs. benzo[ghi]perylene.

To overcome these constraints, in our work all distributions were investigated applying similar methodologies to collect and characterize, in turn, emission exhausts, suspended particulates and dusts. The results were examined in the light of scientific literature dealing with this topic.

Non-polar fraction. Non-polar fraction of POM is comprised of a handful of numerous groups, each comprising sub-groups. They are n-alkanes, alkylated mono-aromatics and biphenyls, n-alkenes, branched and cyclic-aliphatic hydrocarbons. Among them, attention has paid overall on n-alkanes (linear homologues); alicyclic compounds were investigated as tracers of petrol products, and branched alkanes as markers of tobacco smoking.

The saw-teeth distribution of high-molecular-weight n-alkanes has been associated to high vegetation [Eglinton et al 1962, Gelpi et al 1970, Simoneit and Mazurek 1982]. Indeed, biogenic synthesis leads to preferential generation of even C-numbered fatty acids; acids tend to loose CO_2 through the natural process of decarboxylation, hence odd-C numbered n-alkanes are formed (or alkenes, in the case of unsaturated precursors). Since this phenomenon is more evident with regard to high-molecular-weight homologues, the most used parameter rating the impact of (high) vegetation is Carbon Preference Index (CPI_{25}) [Alves et al 2001, Pio et al 2001, Omar et a 2007], obtained by computing $\geq C_{24}$ n-alkanes according to the following formula, where C_n means the term with n carbon atoms:

$$CPI_{25} = \frac{C_{25} + C_{27} + C_{29} + C_{31} + C_{33} + C_{35}}{2*(C_{24} + C_{26} + C_{28} + C_{30} + C_{32} + C_{34})} + \frac{C_{25} + C_{27} + C_{29} + C_{31} + C_{33} + C_{35}}{2*(C_{26} + C_{28} + C_{30} + C_{32} + C_{34} + C_{36})} \qquad (1)$$

By contrast, a mono-modal distribution with maximum centered between C_{19} and C_{26} is typical of petrol-derived exhausts; in this case, CPI_{25} values range from 0.6 to 1.3 [Simoneit 1984, Perrone et al 2014]. In fact, CPI_{25} up to >10 and $\approx$1 have recorded, respectively, in rural regions and at rush traffic sites; in most cases a combination of the two distribution is observed as the signature of the twin fingerprint (see Figure 1).

Figure 1.

Further parameters have been derived, all of them aimed at highlighting the impact caused by vegetation. They are: *i)* the homologue (C_{max}) corresponding to maximum concentration in the distribution; and *ii)* the percentage of natural waxes (NW%) [36, 63]. The NW% rate is provided by the formula:

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

with the foresight of setting each term at numerator equal to zero whereas its actual rate results <0.

Analogous CP indexes were formulated over wider C number ranges or limited to the lighter homologues (<C_{25}), starting from n-C_{11}. Though affected by uncertainty due to hydrocarbon volatility, light CPIs, combined with isoprenoids and $C_{max} = C_{15}/C_{17}$, allow investigating the possible impact of marine (algae, plankton) and micro biota [Fisher et al 1972, Horikawa et al 2010, Wang et al 2010]. On the other hand, the prevalence of even-C homologues was sometimes observed [Kuhn et al 2010]; this finding was explained as the signature of action of bacteria and microorganisms; in this case, the n-alkane distribution within the whole group could show the prevalence of even homologues in the light range, and of odd homologues in the weigh range. Finally, the relative abundance of petrol components (e.g. pristane and phytane) compared to n-alkanes was considered to highlight the vehicle emission impact [Hamilton et al 1984, Alexandrino et al 2019, Alkhafaji 2021].

Until recently, scarce attention was paid to unsaturated hydrocarbons with regard to pollution source reconciliation. Nevertheless, in a study conducted by our team over hundreds of PM and dust samples collected in Italy, Algeria and Tunisia three distinct models were observed relatively to non-polar fraction of POM, overall for congeners $\leq C_{20}$. They were: *i)* the predominant presence of alkanes (n-alkenes negligible); *ii)* the prevalence of n-alkenes (usually dropping from C_{12} and C_{14} down to C_{20}); and *iii)* a mixed behavior (see Figure S1 in Supplementary Material).

Though no exhaustive explanation has been provided for this pattern, however it could originate from direct emission of even n-alkene homologues or/and twin decarboxylation of unsaturated α,ω-diacids. Anyway, this finding seems to merit further investigation, overall because of possible links with anthropogenic or natural nature of sources. Finally, semi-volatile homologues (from C_{20} to C_{26}) were detected in samples probably influenced by tree or bee wax emission [Guenther et al., 1995; Fine et al., 2004].

The alternative occurrence of long-chain odd iso-alkanes and even anteiso-alkanes is ascertained as typical of tobacco leaf burning and detectable in both primary and secondary smoke in interiors [Kavouras et al., 1998] (Figure 2).

Figure 2.

According to that, we introduced two indexes tentatively able to parameterize the impact of smoking on the environment. They are:

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

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

where iC_n, aC_n and nC_n indicate iso-, anteiso- and normal alkanes with n carbon atoms in the molecule.

At this regard, we computed the concentration ratios over the whole C_{29}-C_{34} range to reduce uncertainty associated to small changes in emission profiles of other sources. To verify the affordability of this approach, TSI and AICR rates were calculated for groups of airborne PM and dust samples collected indoor and outdoor at urban and rural sites. The results are shown in Table 1. TSI rates ranged from 0.05 to 1.30, the minimum typical of remote sites and the maximum found at locations heavily affected by tobacco smokes. Hence, the impact of smoking fumes in outdoor air in the cities could be put in evidence (this looks in agreement with the general occurrence of nicotine [Rabhi et al 2018, and references herein]). Worth of note were the TSI and AICR rates in the dust and at the balcony of smoker house (Table 1), which confirmed the contribution of tobacco smoke indoors and nearby outdoors. Though extensive investigations are necessary to confirm this approach, however the molecular signature of iso-, anteiso- and linear long-chain alkanes seems more attractive than nicotine and its derivatives to trace tobacco smoke, thanks to lower volatility and decomposition rate of non-polar aliphatics.

Table 1.

Finally, the occurrence of squalene and squalane was assigned to action of marine organism, while abietane and homologues were associated to coniferous emission [Simoneit and Mazurek 1986, Fine et al 2004]. Table 2 provides a synthetic overview of what discussed above.

Table 2.

Branched and cyclic hydrocarbons affect atmosphere and emissions because they form, as complex blends, the bulk of manufacturing of petrol industry, e.g. fuels (steranes, hopanes; see Figure S1 in Supplementary Material) [Xiao et al 2019]. For instance, in the non-polar fraction gas chromatographic profile of POM, up to two humps of "unresolved mixture" underlie to the n-alkane sequence, as markers of fuels (lighter chemicals) and lubricating oils (heavier components) (Figure 3). Noteworthy, the vehicle emission profile depends on the engine working conditions; in fact, the relative importance of hump increases in unregulated driving/fueling regimens, e.g. during cold starts.

Figure 3.

Polycyclic aromatic hydrocarbons. The general concern of PAHs takes origin from the ascertained toxicity in terms of carcinogenic and mutagenic power as well as of co-promotion of hearth morbidity and premature death [Collins et al

1998, European Parliament and Council 2005, IARC 2012]. Since the PAH fingerprints show wide variability, the chance of associating the chemical imprinting with the nature of emission was widely investigated. At this regard, it is worth to remark that the true composition profile of emission exhausts does not correspond to those usually observed in PM and dust [Kim et al 2009, Tobiszewski and Namiesnik 2012, Keyte et al 2013]. Indeed, most of the PAH budget comes from organic matter burning (e.g., fires, fuel combustion), so the compounds are released overall as vapors; afterwards, PAH condensate onto (fine and ultra-fine) particles of carbonaceous nature, and share their fate (e.g., deposit or move across atmosphere) [Simoneit 2002, Medeiros and Simoneit 2008, Ravindra et al 2008, Lammel et al 2010]. The gas/particle equilibrium developing on particle surface is dynamic and affected by reactivity of congeners, nonetheless the principal PAHs (e.g., those included in the list of priority pollutants [88]) are classified among persistent toxicants [USEPA 1993, MacKay and Callcott 1998, Lodovici et al 2003, Cao et al 2019].

Only a handful of PAHs, as individuals or sub-groups, have been associated to specific sources. Among them, the most important are retene (1-methyl,7-isopropylphenanthrene), benzo[ghi]fluoranthene, and dimethyl/ethylphenanthrene [Tong and Karasek, 1984; Benner et al., 1995; Shen et al., 2012]. The first one is typical of wood, the second looks relatively rich in diesel and gasoline exhausts, and the third occurs as mixture of isomers with very different profiles for vegetation and fossil fuel burning (Figure 4). On the other hand, the detection of cyclopentapyrene, benzo[b]anthracene and anthanthrene, known as fast degrading, highlights the presence of very fresh exhausts [Kim et al 2009].

Figure 4.

Due to contemporary presence of a number of PAHs, a rather common attempt approach aiming to draw insights about the nature of emissions sources is based on the analysis of the concentration ratios of individual substances, chosen as diagnostic [Ravindra et al 2008, Katsoyiannis et al 2011, Katsoyiannis and Breivik 2014]. The most used concentration ratios are FA/PY, BaA/CH, IP/BPE, BaP/BPE, and BaP/BeP; besides, PHE/AN, Σ(methyl-PHE)/PHE and parent-PAHs/ Σ(PAHs) (including alkyl-substituted) are examined. Table 3 provides a list of pairs of PAHs currently examined, and the rates assigned to the principal categories of emission sources. The lack of precise rates leads to consider intervals of critical values, as well three or four pairs of substances.

Table 3.

Though the information obtained remains rough and unaffordable to quantify the contribution of each source to pollution, however it aids recognizing the main sources and putting in the evidence the aftermaths of oxidants action on emissions. This is relevant when final products exceed in toxicity the respective parent PAH direct emission (e.g., quinones and lactones vs. native hydrocarbons) [Durant et al 1999].

Nitrated polycyclic aromatic hydrocarbons (NPAHs). NPAHs gained concern when dedicated studies demonstrated that emissions contain many congeners of this group [Hoekman 1992, Zielinska et al 2004, Liu et al 2010]. These efforts based its rationale in the huge increment of diesel engine vehicles during '70s and '80s of the last century, promoted by tax benefits; indeed, diesel engines were recognized as major sources of NPAHs and 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 were ascertained as mutagenic and cancer promoters [Gbeddy et al 2020]. Attention was

paid overall to a list of NPAHs whose contribution to toxicity of air particulates was even estimated; they were nitrated derivatives of naphthalene, fluorene, anthracene, fluoranthene, pyrene, benz[a]anthracene and chrysene.

Figure 5.

Nevertheless, NO_2-position isomers associated to PM did not correspond exactly to those affecting emissions. In particular, 2-nitrofluoranthene and 2-nitropyrene were commonly absent in exhausts, and their existence was attributed to in-situ reactions developing in the atmosphere according to the following scheme (Figure 5A/B). Hence, the fingerprint of the nitrofluoranthene/nitropyrene subgroup was identified as a tool to parameterize the relative importance of direct emission and action of oxidants. Taking in account the gross nitration rate of compounds starting from precursors, it was suggested that photochemical reactivity prevailed vs. direct emission when the 2-NFA/1-NPY ratio exceeded the value of 5 [Pitts et al, 1985].

Fatty acids and alcohols, polar compounds. Analogously to linear alcohols, 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 acids reveals the clear prevalence of even carbon atoms in the molecule, and the corresponding carbon preference indexes (ACPI), formulated similarly to n-alkanes, can exceed the rate of ten. Other sources display analogous profiles; e.g., vehicle exhausts hold A_{12}-A_{22} acids (i.e., straight-chain homologues with 12÷22 carbon atoms), and distribution profile peaks in the correspondence of A_{16} and A_{18}, though appearing less pronounced. Biogenic sources can distinguish looking to the ACPI rate, and especially to relative abundance of medium- and long-chain homologues. Usually, apart from palmitic (A_{16}) and stearic (A_{18}) homologues, the fatty acid profiles show a secondary maximum in the ranges A_{20}÷A_{24}, or >A_{25}; the lighter ones are associated with microbiota, small plants, softwood trees, and the latter to high plants, hardwood trees [Gelpi et al., 1970]. Besides, with microorganisms ACPI rates result lower, due to meaningful occurrence of odd-carbon acids A_{15}, A_{17}, A_{19} and 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 a minor emission of vegetation and show the usual even-to-odd carbon prevalence, except for <DA_7 homologues, which enjoy of important anthropogenic sources; nevertheless, azelaic acid (DA_9) looks abundant in aged air parcels, as by-product of oleic acid decomposition [Balducci et al 2014, Kawamura and Bikkina , 2016, Ren et al 2020].

Though broadly considered as originated by vegetation, linear alcohols, 2-ketones, aldehydes, fatty acid methyl esters and nitriles have not extensively investigated as source tracers of suspended particulates. Linear alcohols exhibit a behavior parallel to fatty acids and look as primary components of organic particulates in rural regions [Simoneit and Mazurek 1982]. Finally, many sterols are associated to vegetation as components of epicuticular waxes (e.g., sitosterol, stigmasterol, amyrins), while cholesterol looks as a tracer of meat cooking [Cass 1998, Carreira et al 2009].

A set of polar organics, including nicotine and its derivatives, e.g. cotinine, have been proposed as specific tracers of exposure to tobacco smoke (first, second and third-hand) [Hecht 1999, Hammond et al 1987, Daisey 1999, Apelberg et al 2013, Blanchard et al 2014].

Organic halides. The most investigated groups of halides in the environment are probably polychlorobiphenyls (PCBs) and polychlorinated dioxins and furans (PCDD/Fs) [Barbas et al 2018]. PCBs were important industrial products as

finding 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. Despite PCBs and PCDD/Fs have been banned since long time, both groups continue affecting the environment [Ngo et al 2020]. Factory syntheses of PCBs lead to blends characterized by various average percentages of chlorine, which sometimes could aid in highlighting the impact of suspected sources of pollution. Due to different ability of congeners to persist to degrading agents and dissolve in waters and lipids, the molecular fingerprints of PCBs and PCDD/Fs change with time and emission kind [Di Guardo et al 2017, Ngo et al 2018, Ngo et al 2020]; for instance, distinct PCDD/Fs patterns were observed for vehicle exhausts and steel mill fumes.

Polysaccharides. The occurrence of numerous organic substances in the environment looks linked with biomass burning in general, and specifically to some tree species [Oros and Simoneit 2001a/b, Oros et al 2002]. Many chemicals are by-products of lignine (methoxyphenols) [Hawthorne et al 1988, Hays et al 2005], as well as of dehydration-polymerization of carbohydrate molecules (levoglucosan, galactosan, mannosan, inositols). Levoglucosan in particular, adopted as tracer of wood burning, allowed to demonstrate that even metropolitan and megalopolis downtowns undergo the impact of this kind of emission, owing to the generalized use of wood for heating and cooking [Fine et al., 2004]. 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 cities and industrial districts [Pomata et al 2014, Perrino et al 2019, Ren et al 2020].

Conclusions

Chemical fingerprints of organic contaminants affecting airborne particulates, comprised of individual markers and, more often, distribution patterns within the homologue groups, provide preliminary but suitable information about environmental toxicity and nature of emissions. When integrated into extensive statistical approaches, molecular signatures allow assessing the relative importance of sources and put in the evidence links among individual substances, which can help in optimizing the strategies to control air pollution and mitigate the toxicants impact.

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Table headings

Table 1. Rates of TSI and AICR indexes of non-polar fraction associated to airborne particulates and settled dust. The amount of sites for each group is reported between parentheses. Site types: Lazio, urban and rural; Italy and Algeria, urban; SH, NSH and school: urban.

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

Table 2. Indexes describing the n-alkane percent distributions, typical of emission type.

Table 3. Rates of the principal PAH concentration ratios used as diagnostic to draw indication about the type of source.

Figure captions

Fig. 1. GC-MS profiles of the non-polar fraction (m/z = 85) of PM_{10} samples collected at four sites variously influenced by emission sources. A) road traffic site; B) rural region; C) urban location (city park).

Fig. 2. GC-MS profiles (m/z = 85) of dusts collected in interiors. A) private house, smoker apartment; B) waiting room, public hospital.

Fig. 3. GC-MS profile of the non-polar fraction of diesel exhaust. A) total ion current signal; B) ion trace corresponding to m/z = 85 (typical of n-alkanes); C) ion trace corresponding to m/z = 95 (typical of branched alkanes). Both a and b humps are present in the UCM.

Fig. 4. GC-MSD profiles of PAH compounds affecting the suspended particulates of Rome and Leonessa, Italy. A) Dimethyl/ethyl-phenanthrenes in Rome downtown, winter; 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; E) Retene in Leonessa, winter (sample 2)

Fig. 5. Ways of nitrofluoranthene/nitropyrene isomers' formation leading to occurrence of these contaminants in the atmosphere. A) fluoranthene; B) pyrene

Supplementary Materials:

Figure S1. GC-MS profiles (reconstructed ion chromatograms) of non-polar fraction extracted from particulate matters. 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).

Table 1.

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

Table 2.

index	petroleum	algae	microorganisms	high trees	vegetation	anthropogenic
C_{max}	$C_{16}\sim C_{21}$	$C_{17}, C_{19}, C_{21}, C_{23}$	C_{16}, C_{18}, C_{20}	C_{29}, C_{31}, C_{33}	C_{25}, C_{27}, C_{29}	$C_{16}\sim C_{23}$
CPI_{25}	0.7-1.3		>1	>10	>3	0.8-1.3
CPI_{11}	0.8-1.2	> 1.0	< 1.0			
NW%	~0			>75	>75	~0-30

Table 3.

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

Fig. 1
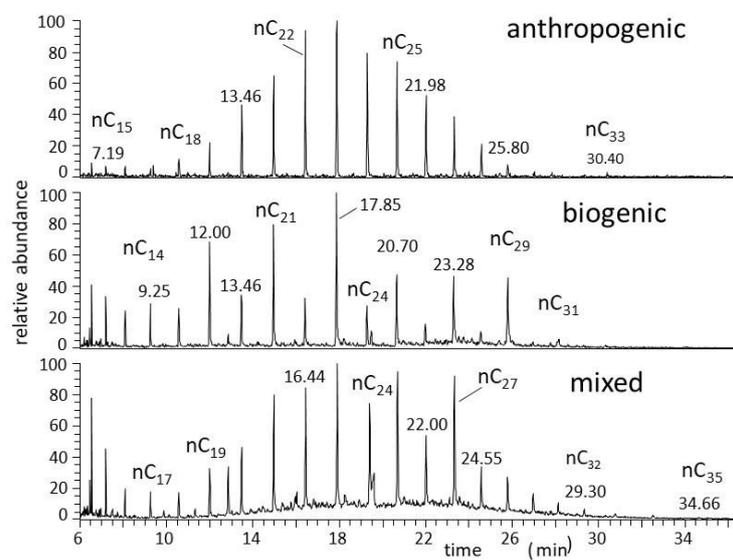
Fig 2.
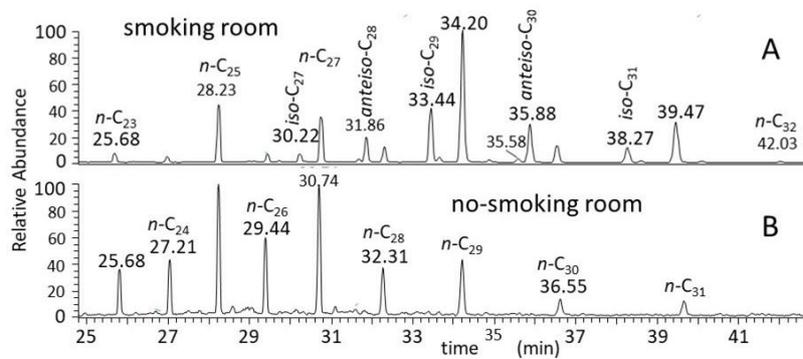
Fig. 3.
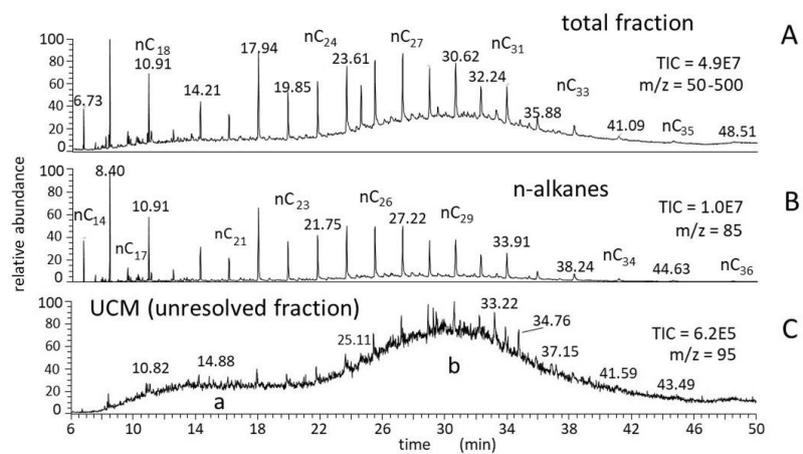
Fig. 4.
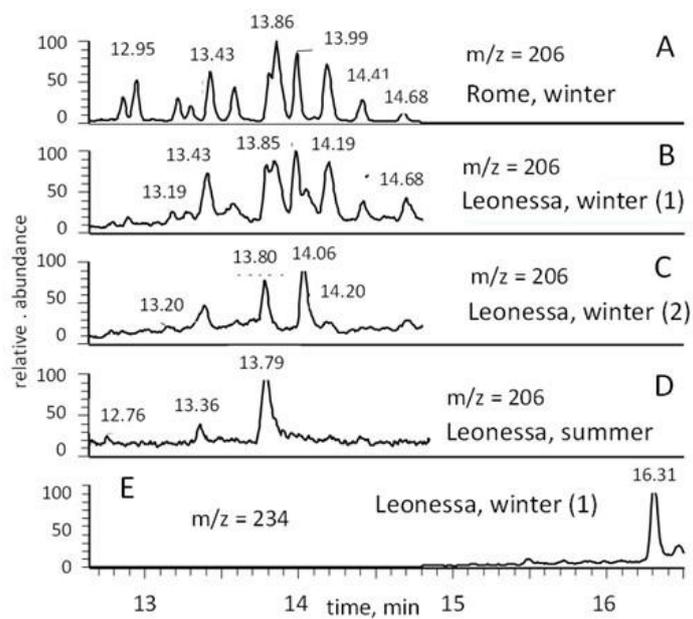
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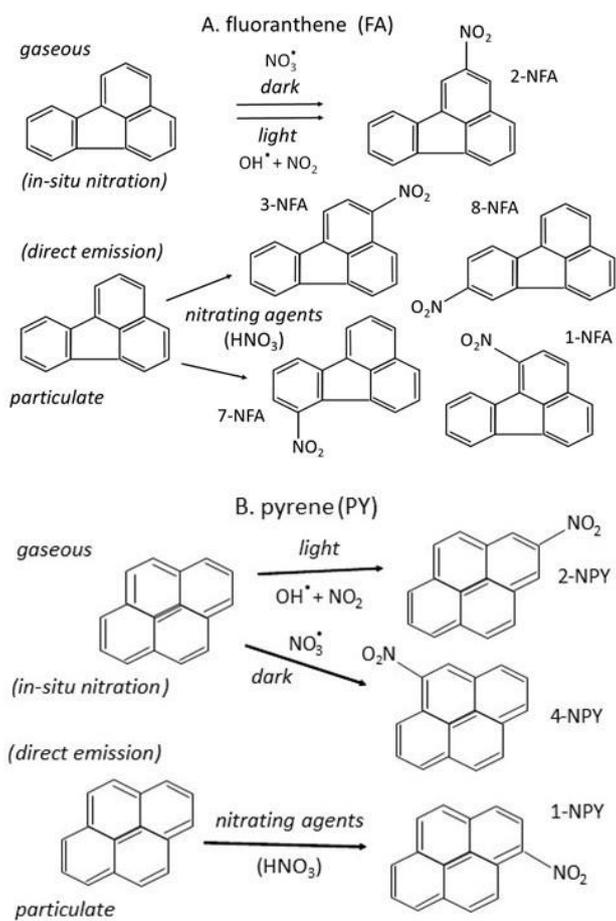
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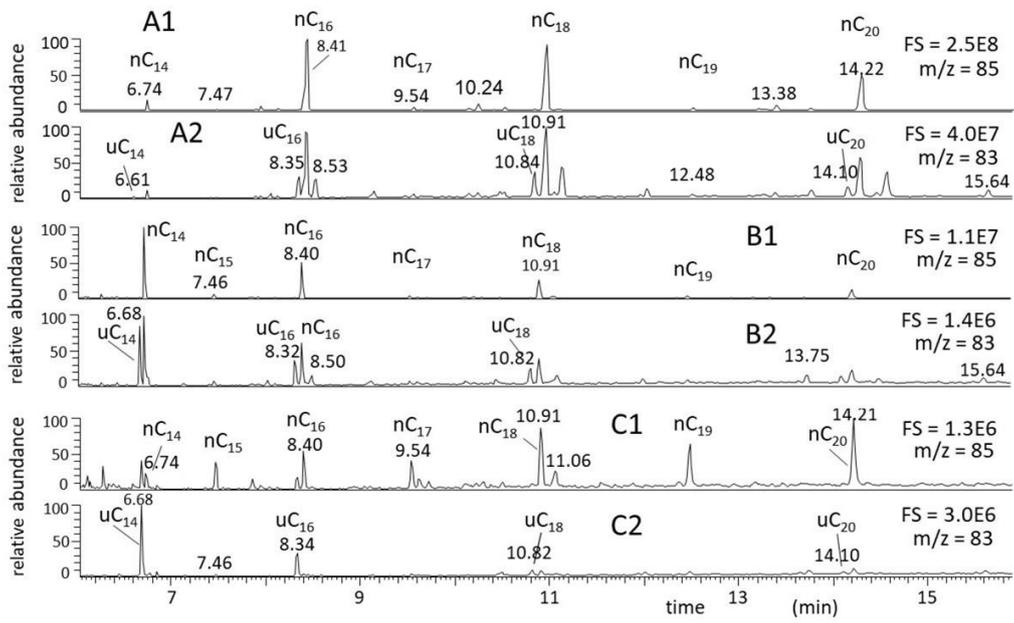
Figures
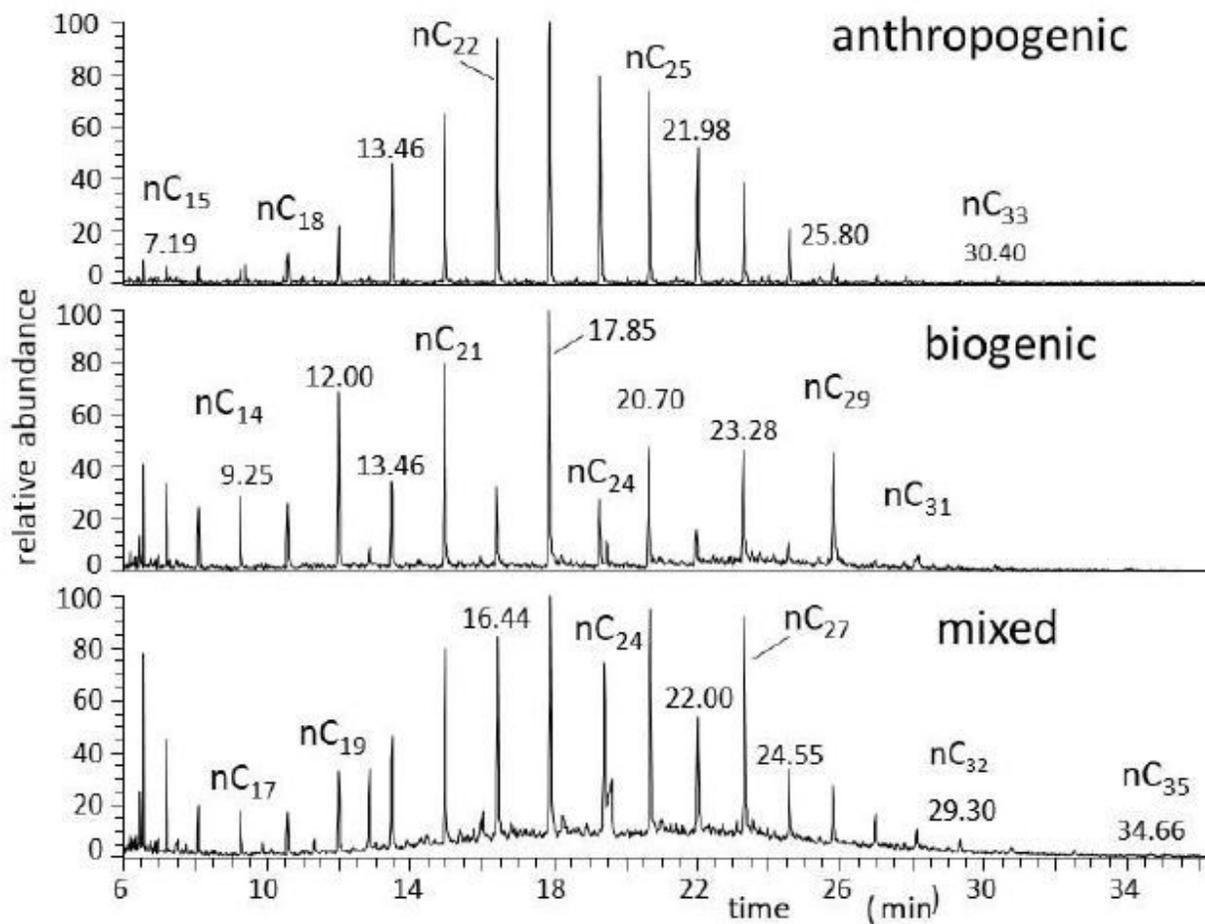
Figure 1

GC-MS profiles of the non-polar fraction (m/z = 85) of PM10 samples collected at four sites variously influenced by emission sources. A) road traffic site; B) rural region; C) urban location (city park).
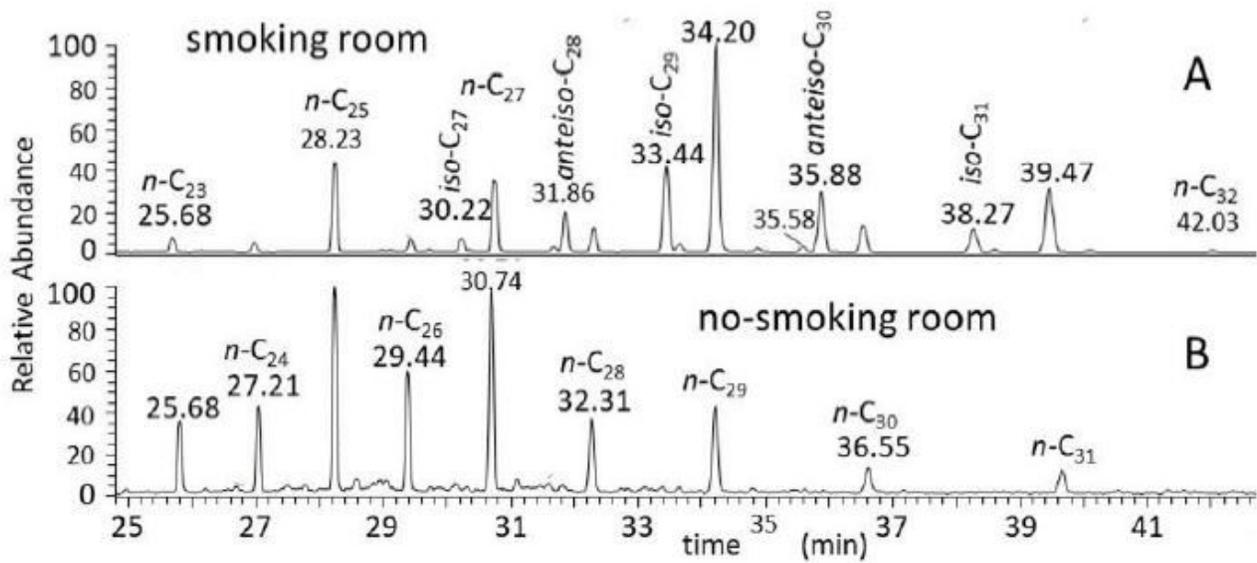
Figure 2

GC-MS profiles (m/z = 85) of dusts collected in interiors. A) private house, smoker apartment; B) waiting room, public hospital.
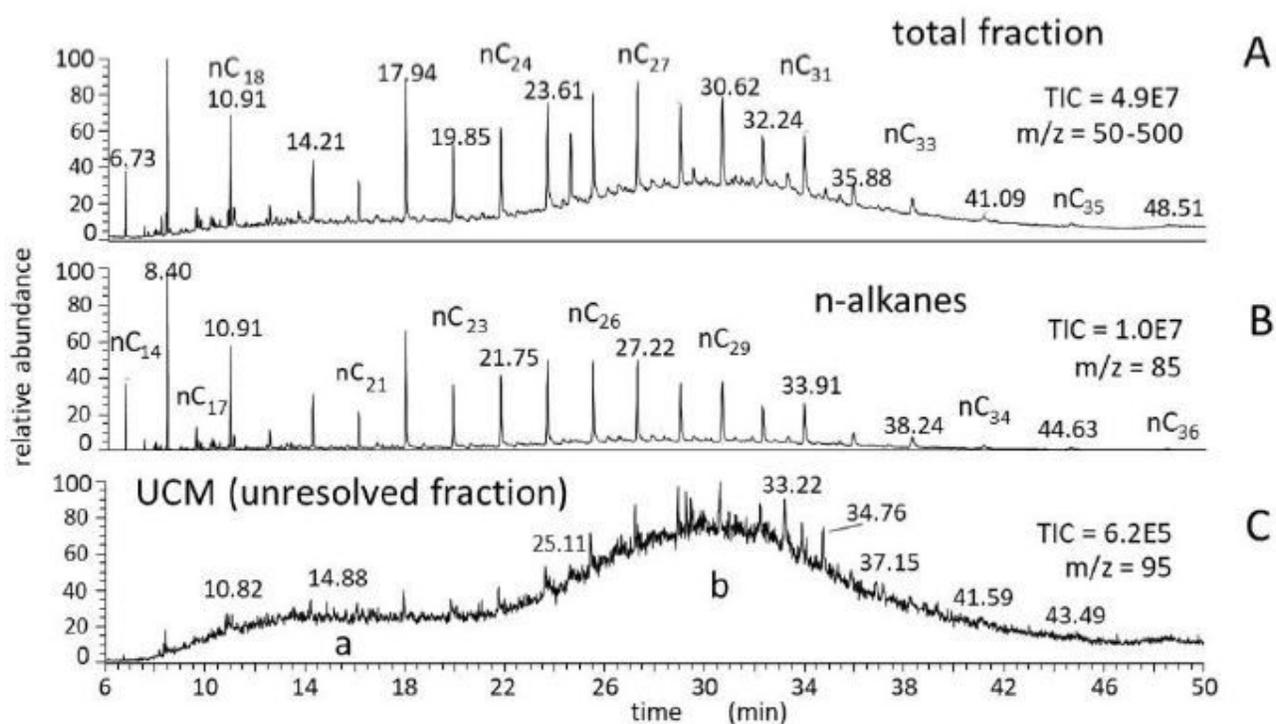
Figure 3

GC-MS profile of the non-polar fraction of diesel exhaust. A) total ion current signal; B) ion trace corresponding to m/z = 85 (typical of n-alkanes); C) ion trace corresponding to m/z = 95 (typical of branched alkanes). Both a and b humps are present in the UCM.
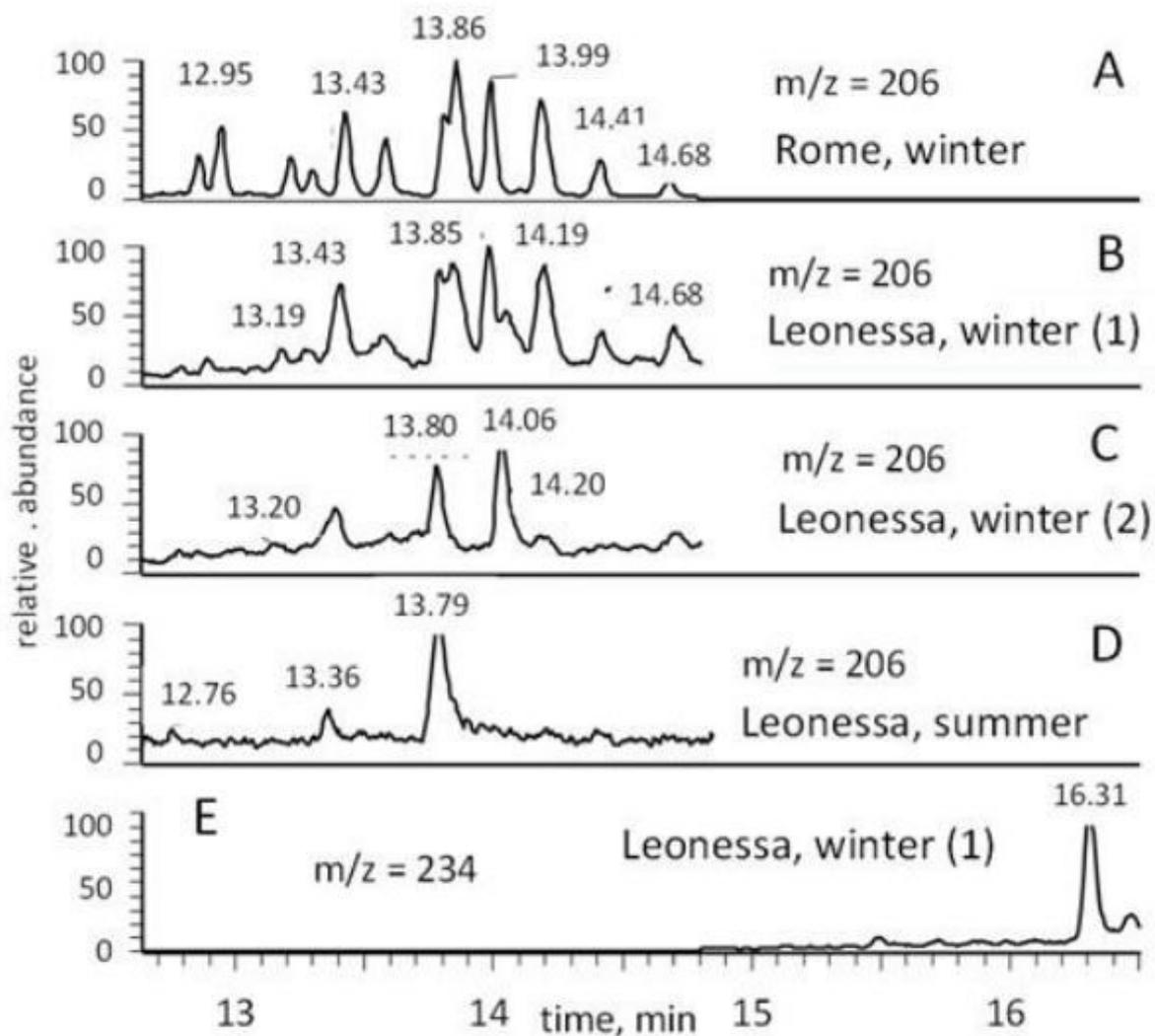
Figure 4

GC-MSD profiles of PAH compounds affecting the suspended particulates of Rome and Leonessa, Italy. A) Dimethyl/ethyl-phenanthrenes in Rome downtown, winter; 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; E) Retene in Leonessa, winter (sample 2)
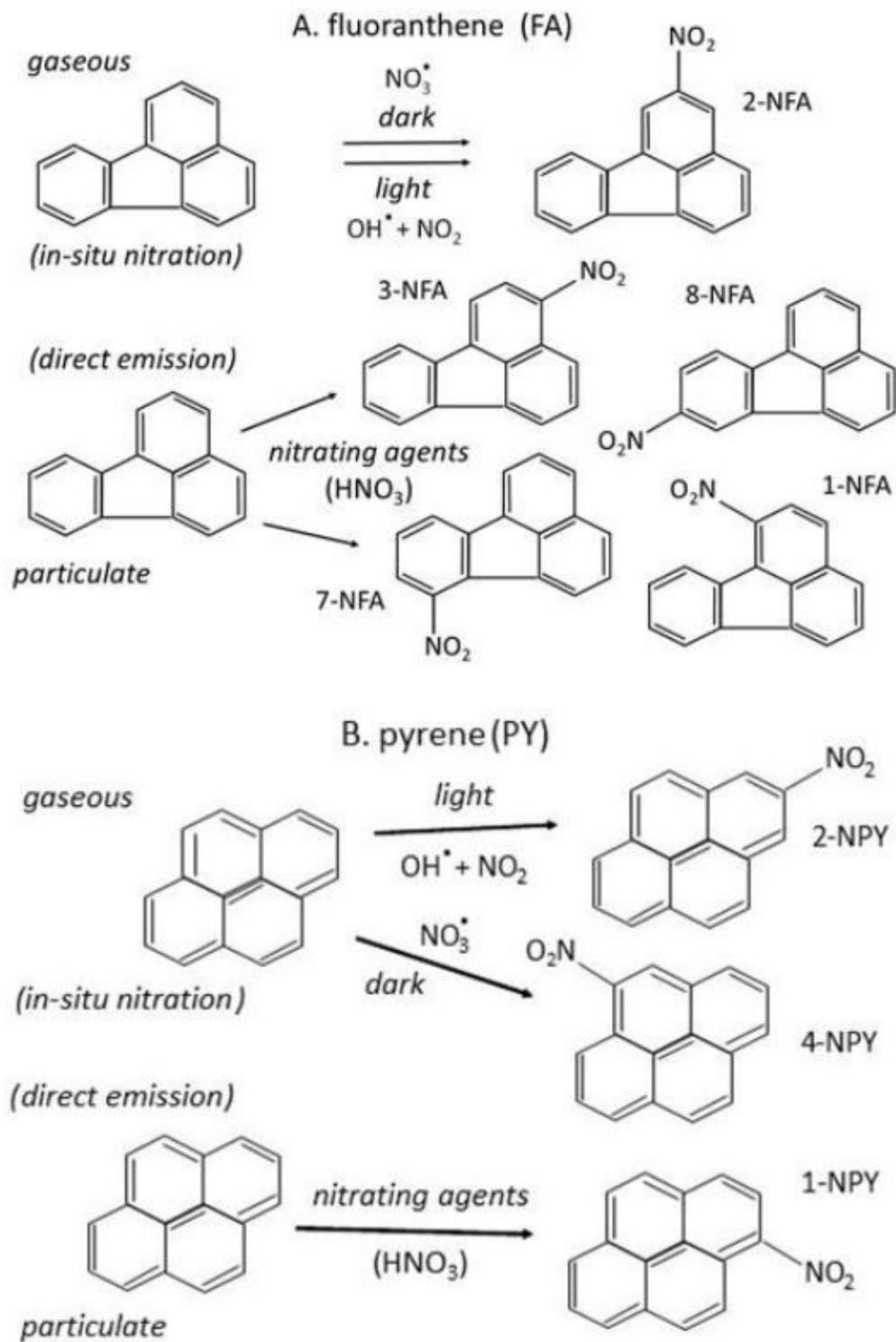
Figure 5

Ways of nitrofluoranthene/nitropyrene isomers' formation leading to occurrence of these contaminants in the atmosphere. A) fluoranthene; B) pyrene

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- FigS1.jpg