Analytical method, pattern and sources of polycyclic aromatic hydrocarbons (PAHs) in the stone of the Temples of Agrigento (Italy)

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ABSTRACT

This study shows the extraction and analytical conditions for the determination of polycyclic aromatic hydrocarbons (PAHs) in the stone of archaeological and historical interest. The aim of this research was to determine the concentrations, distribution and the main sources of PAHs present in the surface layer of stone of the Temples of Agrigento. Together with PAHs, we analyzed sulphates and nitrates since it has been demonstrated that these are very destructive salts that play an important role in the deterioration of stones. Total PAHs at different sites of the Valley of Temples at Agrigento varied from 18 to 84 µg/kg. Analyses were performed by GC–MS. The relative abundance of molecular weight PAHs, together with the PAHs compound ratios and supported by the total index (by us proposed), demonstrate that the most samples in Hellenistic Agrigento historical buildings owe their PAHs to a predominant single mode of origin, i.e. anthropogenic combustion processes. The same origin of PAHs pollution was confirmed by the good correlations existing between total PAHs concentrations and the content of sulphates and nitrates of the analyzed samples.

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1. Introduction

Since the last century, the degradation of natural and artificial stones has been accelerated by increased air pollution, essentially caused by sulphur and nitrogen oxides as well as hydrocarbons which are emitted into the atmosphere by sources related to industry, transportations and heating [1]. Also biological activity in the surface layers of the material contributes to the weathering of stones in monuments [2]. One aspect of the weathering process is the formation of thin surface layers or, in some cases, black coloured gypsum crusts on the stone of buildings [3]. Surface layers are the areas where atmospheric depositions accumulate along with the products of the chemical transformation of materials. Dust and soot have often been blamed for the dark colour of the weathered surfaces. The surface layers not only impair the aesthetic aspect but they also initiate destruction of the stone surface by exfoliation. Their chemical composition varies from one site to another. Physical and chemical weatherings have been largely investigated [4,5], but, only a limited amount of knowledge is available regarding the organic compounds present on the surface layer [3,6,7] material.

It is known that fluidized beds of limestone have been successfully used to remove polycyclic aromatic hydrocarbons (PAHs) and it seems that there is an effect not only of calcium carbonate but also of the porosity of calcite [8].

The principal aim of this study was to determine the concentrations, distribution and the main sources of PAHs present in the surface layers of stone of some historical buildings located in the Valley of the Temples (Agrigento, Italy) dating from 6th B.C. century to 2nd century A.D.

The interest arises from the fact that air pollution is a major concern in Italy along with the industrial wastes and the traffic congestion in cities all causing pollutants that significantly contribute to environmental damage to cultural heritage and to health. Further, often, during the restoration, operators are exposed [9,10] to dusts of the material that in this case can contain very hazardous substances as PAHs.

Atmosphere often contains many organic pollutants which are related to incomplete fuel combustion in domestic heating, industrial plants and vehicular exhausts, such as alkanes, carboxylic acids and PAHs [11,12].

The interest in PAHs, both from analytical and environmental point of view, lies with the fact that, although most of them have no practical use, they are widespread in all the environmental compartments. They can be found, to different extents of concentration, in atmosphere [12], in water [13], in soil [14], in sediments [15], in food [16,17] and in many matrices [18,19] and show high toxicity levels towards living organisms [11,15].

PAHs are chemicals containing two or more fused benzene rings in a linear, angular or cluster arrangement. They are usually generated under inefficient combustion conditions, such as insufficient oxygen by primary natural sources which are forest fires and volcanic activity, but most of the PAHs released into the environment

arise from anthropogenic sources such as burning of fossil fuels, biomasses (grass, wood, etc.) in petroleum refineries, industrial processes, as a constituent of coal tar and motor vehicle exhaust [20].

The lighter PAHs (2–3 rings) are generally found in the gas phase while the heavier ones are mainly associated with airborne particulates. PAHs with more than three rings are speedily transferred to particles, by adsorption or condensation upon cooling of fuel gas. PAHs are transported in the atmosphere over short and long distances in both gaseous and particulate forms. These compounds, in the environment (air, water, sediments, soils, etc.) are subject to redistribution and transformation processes [21,22]. Atmospheric deposition constitutes the main input of PAHs to soil and to monuments surface [3]. Once absorbed in the materials they accumulate [8] and are likely to be retained for long time due to their persistence and hydrophobicity, especially in the presence of organic matter [15,22,23]. The environmental occurrence of PAHs has been associated with adverse effects on public health [24–27]. The effects of airborne PAHs on both human and environmental health have recently forced the European Union (European Community, 2005) to issue strict regulation with regard to these pollutants [25]. This in turn places heavy demand on efficient monitoring of these regulated pollutants. Owing to their persistency and bioaccumulation, often PAHs have been used as biomarkers for purposes of environmental bio monitoring [11].

In order to get a better insight in the environmental levels and distribution of these compounds, reliable analytical methods capable of measuring a large range of PAHs at low concentrations are required. There are some studies on the concentrations of PAHs in different matrices but information about the distribution of PAHs in ancient building materials is rare [3,7]. Some authors have investigated the factors influencing the accelerated solvent extraction for the analysis of PAHs [28–30]. Martınez-Arkarazo et al. [7], in an integrated analytical approach, characterized several organic compounds (mainly PAHs) by GC–MS. Concentrations higher than 20 mg/kg of total PAHs were measured in the black-crusts of the rain-protected areas. They concluded that the presence of certain PAHs indicated combustion of fuels as the main source of deterioration for the palace house building materials. Pyrolysis-gas chromatography/mass spectrometry was used to study the organic compounds present in weathered building materials from historic buildings and monuments. Different materials were investigated: a black layer from a terracotta statue from the Pardon Gate, Cathedral of Seville; a green layer found beneath a black sulphated crust from the Cathedral of Seville; and a black coating covering the stones of the Old Church of Delft. N-alkanes and PAHs were the main components of analyzed samples [31].

The organic and elemental carbon content in Saxonean sandstones as well as a few microbiological data of black surfaces on historic buildings in Dresden has been obtained during preliminary studies. Organic compounds in the samples after extraction were analyzed by GC–MS. About 150 compounds were detected. Their origin is discussed and correlated with data from the literature about organics in the atmosphere and with the microbiological results [32].

The difficulties of analysis of the environmental matrices are due to their high variability (qualitative and quantitative) and their complexity. It is necessary to check the validity of the analytical method using the material to be analyzed.

Here we report an analytical method for 16 PAHs which adopts and improves previous knowledge and affords better results on the concentration levels and the distribution of PAHs in surface layer of eight samples of stone of the Temples of Agrigento.

The investigations have been performed on the fifteen PAHs recommended by US-EPA as priority pollutants to be monitored in the framework of the environmental quality control [26]. Several

PAHs species have been classified into probable (2A) or possible (2B) human carcinogens by the International Agency for Research on Cancer [27]. Moreover, perylene, non-US-EPA listed PAHs, has been investigated with the aim to obtain additional information on PAHs' origin.

In this work, together with PAHs, the chemical composition of the leachable stone fraction is measured. We quantified sulphates and nitrates in the solution of soluble salts because it has been demonstrated that sulphates are very destructive salts that play an important role in the deterioration of stone. In coastal areas like Agrigento, marine aerosol could be the source of a fraction of sulphate ions.

Nitrates have been investigated with the aim to obtain additional information on PAHs origin.

The pollution related atmospheric SO_2 is also a very common source of sulphates. Particulate derived from fossil-fuel combustion and humidity has been shown to play an important role in the sulphatation of carbonate stones. Particulate appears to contribute to the catalytic oxidation of SO_2 to form SO_3, which successively forms sulphuric acid in the presence of water. Transformation of calcite and dolomite by H_2SO_4 leads to precipitation of gypsum and epsomite blocking organic pollutants on the stone surface.

Nitrogen oxides are gaseous components which react directly with the stone surface by forming acids in the presence of water and oxidising agents. These acids react with the stone to form salts (nitrates and nitrites) which either crystallise out within the stone resulting in damage or they are washed away resulting in a loss of material. Nitrates are more soluble salts and expand less than sulphates, leading to little, if any, damage by this mechanism. Removal of sulphates and nitrates by appropriate cleaning procedures is one of the goals of the restoration techniques.

2. Experimental part

2.1. Laboratory equipment

All glassware and sample containers were thoroughly washed with hot detergent solution followed by rinsing with purified water and acetone (analytical grade), respectively. These were finally kept in the oven at 110 °C overnight. To avoid contaminations of samples, different glassware and syringes were used for standards and for solutions extracted from samples.

2.2. Quality assurance

The procedural blanks were routinely analyzed with samples. Limits of quantification (LOQs) were determined as 10 times the noise level of the chromatogram in blank sample (IUPAC Criterion). LOQs of PAHs were in the range of 0.060–2.0 μg/kg dry weights. The procedure was checked for recovery efficiencies by analyzing uncontaminated samples, preventively obtained by extraction of three samples of stone collected in the Valley of Temples area for 24 h with a mixture dichloromethane–pentane 1:1 and spiked with a known quantity of PAHs standards. The average recoveries ranged from 77% to 105%. The relative standard deviations on the PAHs measurements of recovery are less than 15%.

Per-deuterated PAHs surrogate standards were added to all stone samples to monitor the procedures of sample extraction, treatment and analysis. The mean recoveries of surrogate standards added to stone samples ranged from 72% to 102%. The variation of PAHs concentrations in triplicate analyses of samples was less than 12%. All results were expressed on dry weight basis.

2.3. Chemicals

Analytical reagent grade dichloromethane, pentane (Carlo Erba, Milano) were used as solvents. A PAHs standard solution containing 16 PAHs compounds (100–2000 mg/l) (Mixture SS EPA 610, Supelco, Milano) and perylene standard solution (Supelco, Milano) (2000 mg/l) were used. Solution of surrogates PAHs (anthracene-d_{10} and benz[a]anthracene d_{12}) and that of internal standards (acenaphthene d_{10}, phenanthrene d_{10}, chrysene d_{12} and perylene d_{12}) were supplied by Supelco, Milano.

The calibration stock solution was prepared by a 1:100 dilution of the custom PAHs calibration standard solution. Further dilutions of the calibration stock solution were made to prepare five standards that spanned the expected working concentration range. Four deuterated compounds were used as internal standards: acenaphthene d_{10}; phenanthrene d_{10}, chrysene d_{12} and perylene d_{12} were chosen because of isotopic similarity with the analytes of interest.

2.4. Site and sampling

The historical buildings taken in consideration in this study are situated in the Valley of the Temples in Agrigento (Italy). The Agrigento area is one of the most significant archeological sites in the world and a Unesco world heritage site since 1998.

The material most frequently used in the buildings of the temples of Agrigento is limestone. Most of them show obvious signs of deterioration due to stone alteration, air pollution and lack of maintenance.

The samples were taken, during spring and summer 2007, from the surface of the stones already fallen from archaeological buildings and were collected by scraping off the damage layers or removing fragments; care was taken to ensure that the samples were representative of the single building. A total of eight samples were collected. About 25 g of the dust were placed in plastic bags. The samples were refrigerated (4 °C), avoiding the exposure to light, and taken to the laboratory where they were frozen (−20 °C) until the analysis was performed.

About 2 g of homogenized sample of stone were dried at 105 °C for overnight. The water content was determined by weight loss and was utilized to correlate all the results with dry weight. Before each analysis the samples were finely pulverized in a mortar.

2.5. Extraction of PAHs

Among different techniques, available in our laboratory, and various solvents, tested to find the better extraction method, for the matrix considered in this work, we finally used the Soxhlet extraction because it allowed us to obtain the highest recovery percentage of PAHs [18,28] (Table 1).

About 5 g of pulverized sample was mixed with pre-cleaned (Soxhlet extracted with dichloromethane: pentane 1:1 for 24 h) anhydrous Na_2SO_4 (Carlo Erba, Milano), spiked with 125 μl of a solution containing two surrogate PAHs (anthracene d_{10} and benz[a]anthracene d_{12}) and placed in pre-extracted Whatman extraction thimble.

The samples were extracted in Soxhlet apparatus for 12 h by using the solvent mixture dichloromethane–pentane 1:1. The extracted samples were filtered through pre-cleaned pipette filled with solvent-rinsed glass wool and pre-cleaned anhydrous Na_2SO_4, rinsed and concentrated in a rotary evaporator with the thermostatic bath at $T = 35$ (±0.5)°C. The final volume was around 3 ml. Finally the solution containing PAHs was dried under a weak nitrogen flow. The dry residue was dissolved in 125 μl solution containing the following per-deuterated internal standards in cyclohexane (100 μg/l each): acenaphthene d_{10}; phenanthrene d_{10}, chrysene d_{12} and perylene d_{12}.

2.6. GC–MS analyses

In this research, analyses of all samples were carried out using a gas chromatograph since, our preliminary analyses and literature data [16,28] had determined that not all peaks are well separated using the HPLC technique, for example, benzo[b]fluoranthene from benzo[k]fluoranthene.

Analyses were performed using a Shimadzu mod. GC-17A gas chromatograph equipped with PTE-5 (5%-diphenyl-dimethylpolysiloxane, length 30 m, i.d. 0.25 mm, film thickness 0.25 mm) capillary column (Supelco, Milano). This was connected to a mass spectrometer (Shimadzu, quadrupole detector mod. GC–MS-QP5000) with acquisition data system (Shimadzu, CLASS 5000) operating in selected ion monitoring mode (SIM). The interface temperature was held at 300 °C, the EI source at 300 °C and the electron energy was 70 eV.

Injection of 1 μl sample was performed manually. The instrument was equipped with a split/splittless injector with glass wool injection port liner and splittless time of 2 min. Total flow 20.6 ml/min was used. The injector temperature was maintained at 280 °C. The carrier gas was helium (flow rate 1.4 ml/min). The oven temperature program for the GC was injection at 60 °C (hold 2 min), increasing the temperature with 14.5 °C min^{-1} up to 325 °C.

Helium (99.999%) was used as the carrier gas. The analyzed compounds and the monitored ion masses are listed in Table 1. The first ion shown was used for quantification, and the second as the confirmatory ion.

The surrogate standard solution (0.125 μl) was applied to the sample immediately prior to extraction to afford recovery data for quality assurance purposes. The internal standard solution was added to the sample extract prior to transfer to the GC vial to correct for sample volume and instrument variation. Target and surrogate analytes were quantified against the internal standard belonging to the same group (Table 2).

A total of 5 calibration standards were available to provide a concentration range of 5–100 μg/l. The mean correlation coefficients of the calibration lines from the different MS runs were >0.99 for all compounds, attesting the high linearity of the calibration curve for this concentration range.

The identification of the components of the standard mixture was carried out by comparing retention times of each component of the mixture with those of pure components, analyzed under the same experimental conditions. Identification was confirmed by comparing the spectra of the single components with those stored in the library of the acquisition system. The identification of PAHs in solutions originating from the sample extract was carried out on the basis of previously determined retention times and confirmed using mass spectra. The PAHs in the samples were quantified relative to per-deuterated PAHs added to dry residue.

2.7. Analysis of sulphate and nitrate

Powdered samples were dried at 105 °C until constant weight. The salts solubilisation was achieved by shaking 100 mg of each dried sample in 100 ml of ultra-pure water overnight at room temperature.

Table 1
Results of recovery tests carried out on a mixture of 16 compounds.

Extraction method	Ranges recovery % (mean of three analysis)
Soxhlet	77–105 ± 15
Ultrasound (n-pentane:CH_2Cl_2 = 1:1)	45–69 ± 14
Ultrasound (CH_2Cl_2)	48–71 ± 19

Table 2
List of groups of PAHs formed for analysis, the deuterated internal (underlined) and surrogate (italic) standards employed, the quantification ion, the confirmation ion for SIM GC–MS mode and quantification limits (μg/kg d.w.).

Group	Analytes	Quantification ion	Confirmation ions	Quantification limits (μg/kg d.w)
1	Acenaphthylene	152	76, 151	0.060
	Acenaphthene	154	152, 76	0.095
	Fluorene	166	164, 165	0.65
	<u>Acenaphthene d$_{10}$</u>	<u>164</u>		
2	Phenanthrene	178	188,89	2.0
	Anthracene	178	188, 89	0.28
	Anthracene d$_{10}$	<u>188</u>	<u>188</u>	
	Fluoranthene	202	101, 200	1.1
	Pyrene	202	101, 200	1.0
	Benz[a]anthracene	228	114, 226	0.55
	Benzo[a]anthracene d$_{12}$	<u>240</u>	<u>240</u>	
	<u>Phenanthrene d$_{10}$</u>	<u>188</u>		
	Chrysene	228	114, 226	1.0
	Benzo[b]fluoranthene	252	126, 250	1.2
	Benzo[k]fluoranthene	252	126, 250	0.25
3	Benzo[a]pyrene	252	126, 250	0.28
	<u>Chrysene d$_{12}$</u>	<u>240</u>		
4	Perylene	252	126, 250	0.32
	Indeno[1,2,3-cd]pyrene	276	277, 138	0.15
	Dibenz[a,h]anthracene	278	279, 139	0.15
	Benzo[g,h,i]perylene	276	138,124	0.10
	<u>Perylene d$_{12}$</u>	<u>264</u>		

The obtained supernatants were filtered through 0.45 μm PTFE membrane driven filters (Millipore) by disposable syringe over-pressure, prior to the analyses.

The employed method for sulphates determination was turbidimetric according to the standard methods for water analysis of the American Public Health Association (APHA) [33]. Sulphate concentrations were measured with a UV–vis visible spectrophotometer (Jasco 7800).

Nitrate concentrations were measured by potentiometry using an ion selective electrode (Mettler Toledo S7/120) [33].

3. Results and discussion

The total PAHs concentrations at different stations are shown in Table 3 and Fig. 1. Results are given as mean value of triplicate analyses of each sample. Sum of 16 PAHs at different sites of Agrigento varied from 18 (Kolimbetra) to 84 μg/kg d.w. (Demetra) with a mean of 40 μg/kg.

Sites Kolimbetra and Hellenistic Area, located in the upwind direction of the main urbanized vicinity revealed the lowest of total PAHs concentrations. This was possibly due to less anthro-

pogenic activities in the rural area located in the outskirts of the city. Consequently, in clean environment, as in not anthropyzed areas, lower accounts atmospheric pollutants are available for deposition. While the highest concentrations were measured in station Demetra, an area in proximity of Agrigento city characterized by slow and heavy traffic flow. Also, high PAHs levels (62 μg/kg d.w.) have been measured in station Ercole located in an area, where the traffic is severe and some time slow. The wide range of total and single PAHs concentrations (RSD = 40–108%) indicates heterogeneous levels of contamination in the Valley of the Temples area. Observed PAHs concentrations in this study were much lower than the concentrations (77–9798 μg/kg) reported for the sum of 19 PAHs in Palermo stone monuments [3] and in a palace house in the metropolitan Bilbao [7]. This is due to the fact that Palermo and Bilbao are two cities that are much more populated than the Valley of the Temples and, additionally, the studied monuments in Palermo are located in very narrow streets where the dilution of pollutants is limited and PAHs and other substances (NO$_x$, SO$_2$, particulate, etc.) remain in contact with the stone for long time.

Among individual PAHs, phenanthrene was the most abundant compound at six out of eight stations with con-

Table 3
Concentration (μg/kg d.w.) of single polycyclic aromatic hydrocarbons (mean of three analysis) in stone samples collected on Archeological area of Agrigento.

| Compounds	Demetra	Giunone	Hell area	Ercole	San Calogero	Kolimbetra	Concordia	Esculapio	Mean
Acenaphthylene	0.68	0.35	0.36	0.21	0.40	0.20	0.19	0.48	0.36
Acenaphthene	1.3	0.27	0.28	0.13	0.53	0.15	0.14	0.12	0.37
Fluorene	1.8	1.8	1.4	1.1	3.0	0.6	0.70	2.2	1.6
Phenanthrene	11	12	5.0	7.2	12	2.4	3.5	12	8.2
Anthracene	0.41	0.36	0.28	0.35	0.43	0.32	0.62	1.1	0.49
Fluoranthene	4.8	2.2	1.5	5.6	2.1	1.5	2.4	2.9	2.9
Pyrene	4.3	2.0	1.4	3.6	2.0	1.1	2.2	2.5	2.4
Benz[a]anthracene	3.5	0.8	0.8	4.9	0.31	0.60	1.0	1.7	1.6
Chrysene	5.7	0.74	1.1	5.2	1.0	1.9	2.8	4.7	3.0
Benzo[b]fluoranthene	13.1	1.5	2.1	6.6	3.3	1.6	3.0	3.8	4.4
Benzo[k]fluoranthene	4.5	0.72	1.1	2.8	1.5	0.71	1.2	1.4	1.7
Benzo[a]pyrene	9.7	1.7	2.4	5.4	1.3	0.30	1.6	3.8	3.3
Perylene	7.2	3.2	1.7	4.7	0.50	0.70	0.50	0.84	2.4
Indeno[1,2,3-cd]pyrene	7.3	1.6	1.6	6.3	0.20	2.1	3.4	4.1	3.3
Dibenz[a,h]anthracene	2.3	0.18	0.58	2.4	0.31	0.63	0.88	0.95	1.0
Benzo[g,h,i]perylene	6.2	1.6	2.5	5.2	0.10	3.7	2.6	3.2	3.1
Total PAHs	84	31	24	62	29	18	27	46	40
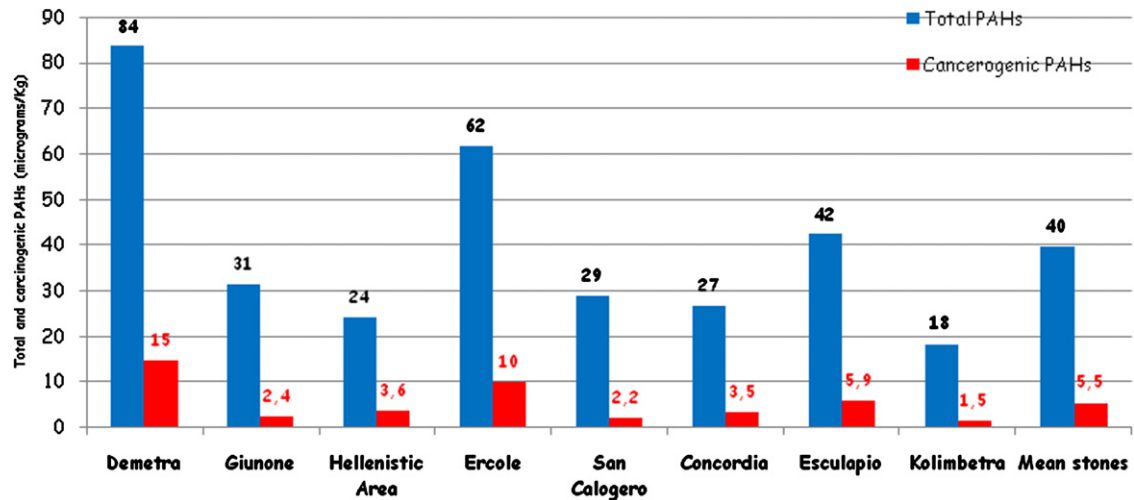
Fig. 1. Total and concerogenic PAHs concentrations (average of three analysis) in μg/kg d.w. in samples of stone.

centration ranging from 2.4 to 12 μg/kg and a mean of 8.2 μg/kg.

Considering the average of the results of all the studied samples, phenanthrene, benzo[b]fluoranthene, benzo[a]pyrene and chrysene are the four most abundant components (Fig. 2). Phenanthrene (3 rings) is always much more abundant than the isomeric anthracene. These experimental evidences are consistent with the composition of urban dusts determined by analysis of several samples of urban particulate [18], where most of PAHs derived from automotive traffic. Only at sites San Calogero and Giunone, predominance of low molecular weight (3 rings) species, was observed. Predominance of 3-ring is not expected in car particulate because of the high volatility nature of low molecular weight PAHs. Low molecular weight PAHs mainly originate from low temperature

processes. The predominance of low molecular weight PAHs in the San Calogero and Giunone samples reflects the presence of significant combustion products from low temperature processes such as biomass burning [30] that, in the Agrigento area, is a common agriculture practice.

Perylene was found at all stations. The most polluted station (Demetra) shows the maximal absolute concentration (7.2 μg/kg d.w.) and is followed in decreasing order by stations Ercole (4.7 μg/kg d.w.) and Giunone (3.2 μg/kg d.w.). However, on a relative basis, perylene accounts from 1.7% to 10% of total PAHs. The origin of perylene is controversial, some authors argue that the marked abundance precludes its pyrogenic origins, in fact, a perylene contribution of more than 10% indicates a diagenic process [34–36]. Perylene is not present or occurs only in a small amount in
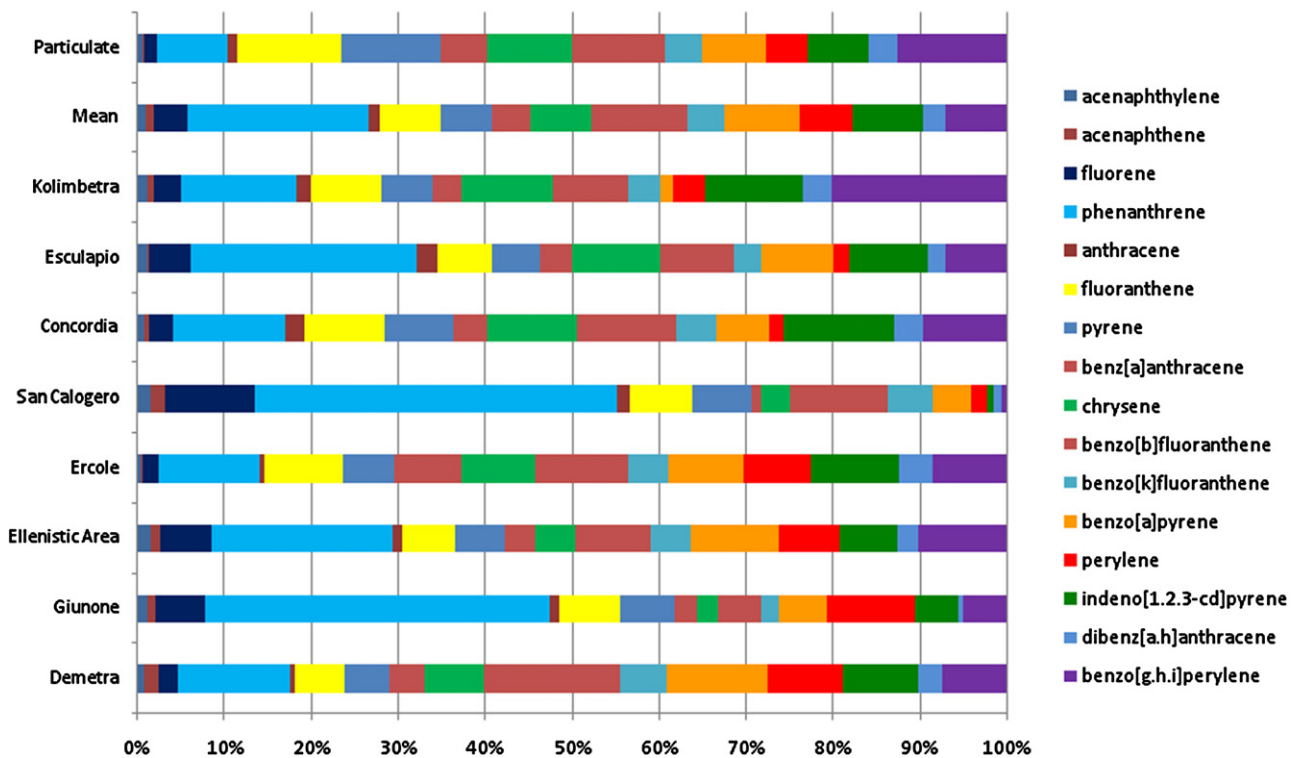

Fig. 2. Distribution of single compounds in stone and particulate samples (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.).

Table 4
Isomeric ratios.

Isomeric ratios/samples	Demetra	Giunone	Hell area	Ercole	San Calogero	Concordia	Esculapio	Kolimbetra	Mean
An/(An + Ph)	0.04	0.03	0.05	0.05	0.03	0.15	0.09	0.11	0.07
Fl/(Fl + Py)	0.53	0.53	0.51	0.61	0.51	0.53	0.53	0.58	0.54
B[a]/(B[a] + Cr)	0.38	0.52	0.43	0.48	0.24	0.26	0.27	0.23	0.35
IP/(IP + B[g,h,i])	0.54	0.50	0.39	0.55	0.53	0.57	0.56	0.36	0.50
Total index	4.7	5.2	4.8	5.5	3.9	5.3	4.6	4.5	4.8

the products of combustion processes, probably due to its thermal instability or reactivity, but there is also significant evidence that it can be produced biologically under anaerobic conditions [37]. Several authors reported PAHs formation through plant and microbial metabolism [38] and showed that wood from forest contained naphthalene, phenanthrene and perylene. Thiele and Brummer [37] reported that biological formation of 3, 4, 5 and 6-ring PAHs was observed after incubation of fresh plant material and of soil mixed with fresh plant material under reducing conditions. Perylene quinones (pigments found in several organisms) are suspected to be degraded to perylene by anaerobic microbial metabolism [36].

In order to assess specific inputs of perylene to the Stone of Temples, the distribution patterns of PAHs were evaluated for the investigated samples and compared with those of the atmospheric particulate sampled at several monitoring stations. Fig. 2 shows that the distribution of perylene in the stones, matches those of atmospheric particulate. Hence, the presence of perylene in the temples must be related to vehicular emissions. There is a good correlation ($r = 0.84$) between total PAHs concentration and perylene content. This evidence suggests that the perylene identified in the samples originates from the same type of emission which contains most of the other PAHs.

In the case of the stone material studied in this research, the perylene cannot have biological origin, because the samples were taken from the exposed to air surface and therefore cannot include reducing environments.

A linear correlation between total PAHs concentration and single compound content was calculated. The values of r for the most representative compounds ($n = 14$) ranged from 0.66 to 0.95. These results suggest that most of the PAHs identified in the samples of stones, originate from the same type of emissions (Table 4).

Of all PAHs analyzed in this context some of them, especially the slightly volatile ones, are not regarded as carcinogenic. Within the remaining PAHs, there are substantial differences of potency in the size of several orders of magnitude. Seven PAHs, B[a]A, Chry, B[b]F, B[k]F, B[a]P, DB[ah]A and IP, have been classified as probable

Table 5
Toxic equivalency factors (TEFs).

Compound	TEF	Compound	TEF
Acenaphthene	0.001	Benzo[k]fluoranthene	0.1
Acenaphthylene	0.001	Benzo[b]fluoranthene	0.1
Anthracene	0.01	Indeno[1,2,3-cd]pyrene	0.1
Benz[a]anthracene	0.1	Perylene	0.001
Fluoranthene	0.01	Dibenz[a,h]anthracene	1
Fluorene	0.001	Benzo[a]pyrene	1
Phenanthrene	0.001	Chrysene	0.01
Pyrene	0.001	Benzo[g,h i]perylene	0.01

human carcinogens by International Agency for Research on Cancer (IARC) [27]. We used the individual compound potency equivalency factor (PEF) relative to B[a]P [17,39] to estimate total carcinogenic PAHs. Benzo[a]pyrene is the only PAH for which toxicological data are sufficient for derivation of a carcinogenic potency factor among all known potentially carcinogenic PAHs.

Concentrations of carcinogenic PAHs are calculated by:

$$TEQ = \sum (PAH_i \times TEF_i)$$

where TEQ is the toxic equivalents of reference compound; PAH_i is the concentration of PAH congener i; TEF_i is the toxic equivalent factor for PAH congener i (Table 5) [17,39].

Calculated total B[a]P$_{eq}$ concentrations at different sampling sites varied from 1.5 µg/kg (Kolimbetra) to 15 µg/kg (Demetra) with an arithmetic mean of 6.1 µg/kg. Total B[a]P$_{eq}$ concentration was highest at site Demetra (Fig. 1) and it was 3 times higher as compared to mean of all sites.

The sulphates and nitrate content at different stations are shown in Fig. 3. Results, expressed as percentage on dry stone, are given as a mean value of triplicate analysis of each sample. Sulphates at different sites of Agrigento varied from 4.0% (Kolimbetra) to 13% (Ercole) with a mean of 8.9% while nitrates ranged from 0.30% (Kolimbetra) to 2% (Demetra).
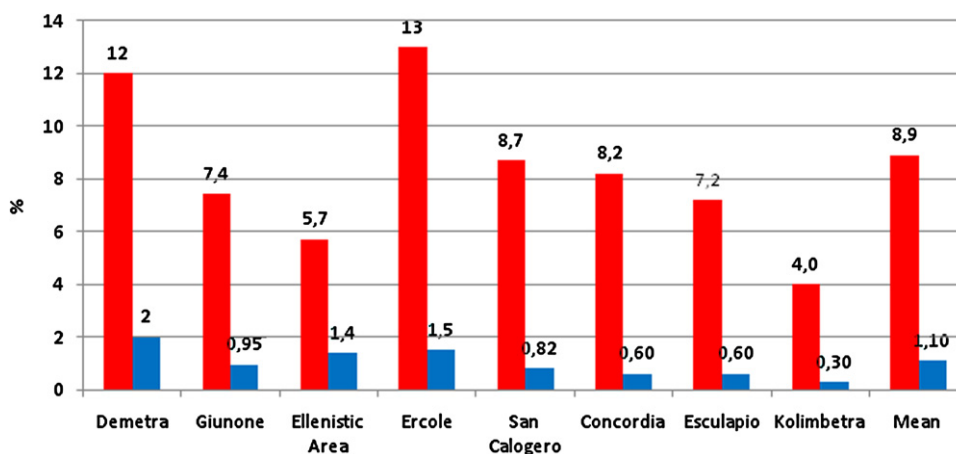

Fig. 3. Sulphate (red) and nitrate (blue) concentrations (%, w/w) in various stones. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)
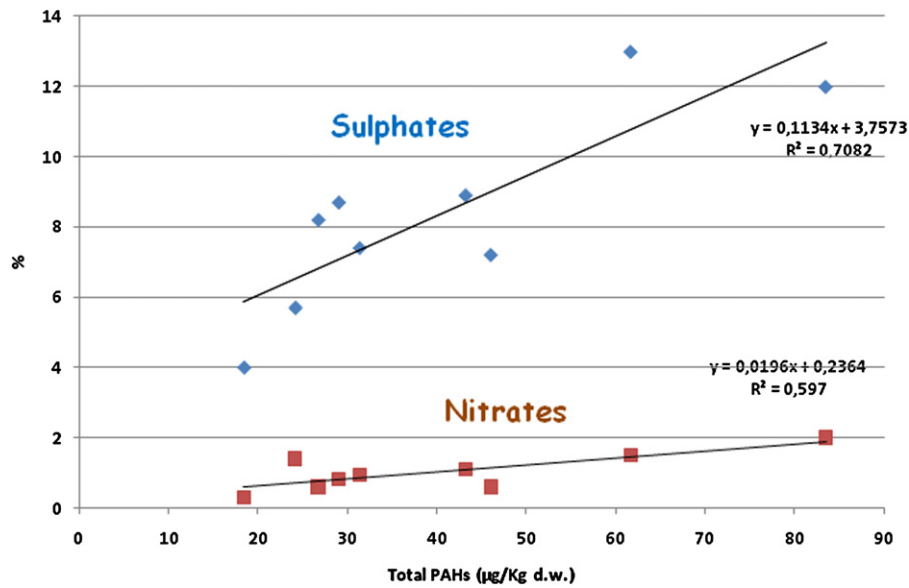
Fig. 4. Concentration of sulphates and nitrates (%, w/w) as a function of total PAH concentration (% µg/kg d.w.) measured in different stones.

With the aim to find a relationship between the content of sulphate, nitrates and the concentration of PAHs determined in the investigated samples, we carried out a linear regression analysis whose results are reported in Fig. 4. The data showed positive linear relationships for all the sites with a correlation coefficient of 0.84 for sulphates and 0.77 for nitrates. From these results, we can suppose that PAHs identified in the collected samples would originate from the same sources that originate the sulphates (combustion of fossil fuels) and nitrates (vehicular traffic). In analyzed samples,

a negligible fraction of sulphate ions could have originated from marine aerosol.

3.1. Sources of PAHs

The molecular patterns generated by each sources are like fingerprints and it is possible to determine the processes that generates PAHs by studying their distribution in samples. Pyrolytic sources are characterized by the occurrence of PAHs over a wide
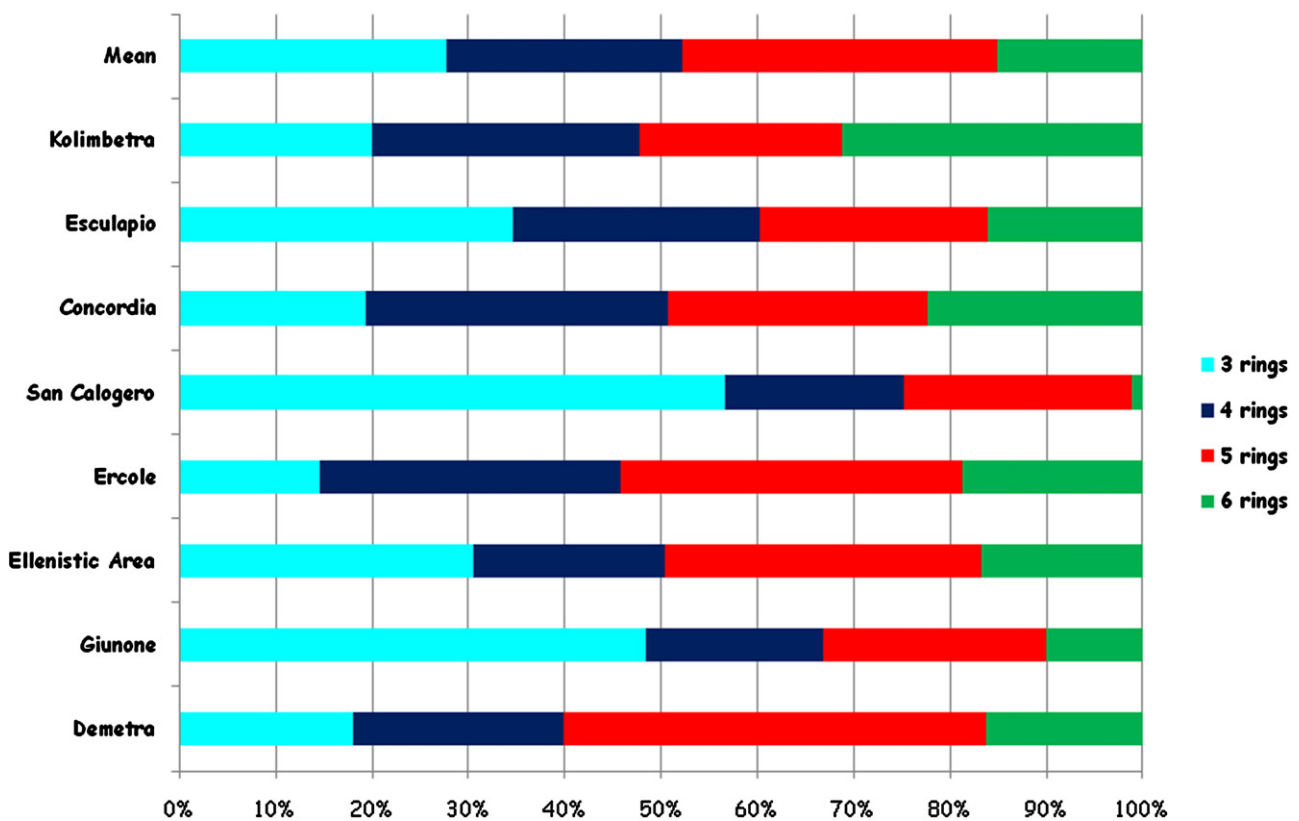

Fig. 5. Concentration of poly-aromatic compounds containing 3, 4, 5 and 6 rings (%, w/w) in different monument stones (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.).

range of molecular weights, while low temperature (petroleum, etc.) sources are dominated by the lowest molecular weight (3 rings) PAHs. Penta and hexa-aromatic compounds are only present at trace levels. If we group the polycyclic aromatic compounds in different classes depending on the number of aromatic rings present in their structure (Fig. 5), it can be observed that PAHs having 3 and 4 rings, found in stones under investigation, contribute about 50% of the total. This evidence suggests that PAHs contamination in the stone might originate mainly from high temperature sources, for example from combustion of fossil fuel.

Sources of the PAHs pollution in the matrix under investigation have been estimated by using distribution indexes relative to concentration ratios of some polycyclic aromatic compounds. PAHs isomer pair ratios have extensively been used to explain the possible sources [3,11,15–20,34,40]. These indexes are based on thermodynamic stability of compounds.

The ratio of anthracene to anthracene plus phenanthrene (An/An + Ph), fluoranthene to fluoranthene plus pyrene (Fl/(Fl + Py)) and benz[a]anthracene to benz[a]anthracene plus chrysene B[a]A/(B[a]A + Chry) have been frequently used in several papers [16,17,20]. PAHs of molecular mass 178 and 202 are normally used to distinguish between combustion and petroleum sources.

For mass 178, an anthracene to anthracene plus phenanthrene (An/An + Ph) ratio <0.10 is taken as an indication of low temperature processes (petroleum) while a ratio >0.10 indicates a dominance of combustion [20].

In our samples, the An/An + Ph ratio varies between 0.03 and 0.15. The average ratio for stones is at or just above 0.10 for only Concordia and Kolimbetra sites (0.11 and 0.15, respectively). The An/An + Ph ratio also is >0.10 in urban particulate samples.

In this study Fl/(Fl + Py) ratio has been used to identify sources of PAHs. Yunker et al. [20] suggested that a Fl/(Fl + Py) ratio <0.4 indicates petroleum input, ratio between 0.4 and 0.5 liquid fossil fuel (vehicle and crude oil) combustion and ratio >0.5 grass, wood or coal combustion. In our study the Fl/Fl + Py ratio also is 0.51 in atmospheric particulate samples. In temples stones, the values of Fl/(Fl + Py) ratio varied between 0.51 and 0.61 indicating combustion as the main PAHs source at the studied sites. The obtained values are in good agreement with the fact that biomass burning in the considered area is a common agricultural practice.

In this study the values of B[a]A/(B[a]A + Chry) ratio varied between 0.23 and 0.52, the mean value was 0.35. The lowest values were found at sites San Calogero (0.24) and Kolimbetra (0.23) indicating that the prevailing input of PAHs was derived from low temperature processes. Yunker et al. [20] suggested that values <0.2 and >0.35 were indicative of petroleum and combustion origin respectively whereas values between these two critical values implied mixed origin e.g. petroleum combustion. Therefore, PAHs in the stone of Valley of Temples sites in Agrigento might be mainly of combustion origin.

IP/(IP + B[g,h,i]P) ratios for our samples ranged from 0.36 to 0.57 with an average value of 0.50. Accordingly to literature data, IP/(IP + B[g,h,i]P) ratios higher 0.50 imply combustion [20]. The lowest value was found at site Kolimbetra (0.36) indicating that the prevailing input of PAHs was derived from low temperature processes.

In some cases, the values of four ratios are not in agreement among them, and considering that, generally, the sources of PAHs in a matrix may be different and occasional, we calculated a total index [18] as the sum of single indices (previously discussed), respectively, normalized for the limit value (low temperature sources-high temperature sources) reported in the literature [20]:

$$\text{Total index} = \frac{An}{(An + Ph)/0.1} + \frac{Fl}{(Fl + Py)/0.4} + \frac{B[a]A}{(B[a]A + Chr)/0.2}$$
$$+ \frac{IP}{(IP + B[ghi]P)/0.5}$$

We assume that PAHs originating prevalently by high temperature processes (combustion) have a total index is >4 while lower values indicate prevalently low temperature sources (petroleum product). The obtained mean value (4.8) (Table 3) confirms that most of the PAHs identified in the stone samples originate from combustion processes.

4. Conclusions

This study shows the extraction and analytical conditions for the determination of PAHs in deteriorated stone. The quantitative method may be favorably applied to many other similar matrices. Under the conditions used through, the recoveries are very good; in every case they are greater than 77% and in most of the cases near 100%. The reproducibility is also satisfactory (relative standard deviation less than 12%).

The data concerning the components due to atmospheric deposition can be summarized as follows:

(a) Sulphate is the main species present in the surface of stone due to the transformation of calcium carbonate determined by atmospheric SO_2, SO_3 and H_2SO_4. The damaged surface layer also embeds the organic substances of atmospheric deposition which play a primary role in the development of deterioration (i.e. patina formation).
(b) The content of nitrates in the samples is lower than those of sulphates because they are very soluble and do not form stable compounds with calcium of the stone;
(c) An organic carbon fraction is mostly composed of PAHs that, generally, are tracers of specific anthropic sources, such as exhaust from vehicles, domestic heating systems, craft activities and emission of agricultural practices.

The wide range of PAHs concentrations found in the different stations of the Valley of the Temples of Agrigento reflects strong gradients of pollution attributable to sources as well as to different degrees of air dispersion.

The relative abundance of high molecular weight PAHs, together with the PAHs compound ratios has demonstrated that the most samples owe their PAHs in Agrigento historical buildings to a predominant single mode of origin, i.e. anthropogenic combustion processes. The same main origin of PAHs pollution was confirmed by a good correlation existing between total PAHs concentrations and the content of sulphates and nitrates of the samples.

The total index, proposed by us, permits to avoid the different responses of single indexes and identify the predominant sources on PAHs in an environment.

It must be emphasized that this work strongly confirms the great dependence existing between the degradation of historical buildings and air pollution.

The study of alteration processes due to atmosphere material interaction is of primary importance for a correct planning of conservation and maintenance of historical buildings. In most cases this mission is assigned to restorers and operators of cultural heritage. Also, the results of this research offer a scientific basis for risk analysis, especially for restorers, caused by carcinogenic PAHs deriving by the stone contamination.

Finally, it seems very likely that the results of the present study on the Valley of Temples may be extended to many historical and archeological sites located in polluted areas.

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