

Polycyclic aromatic hydrocarbons (PAHs) in burning and non-burning coal waste piles

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ABSTRACT

The coal waste material that results from Douro Coalfield exploitation was analyzed by gas chromatography with mass spectrometry (GC–MS) for the identification and quantification of the 16 polycyclic aromatic hydrocarbons (PAHs), defined as priority pollutants. It is expected that the organic fraction of the coal waste material contains PAHs from petrogenic origin, and also from pyrolytic origin in burning coal waste piles. The results demonstrate some similarity in the studied samples, being phenanthrene the most abundant PAH followed by fluoranthene and pyrene. A petrogenic contribution of PAHs in unburned samples and a mixture of PAHs from petrogenic and pyrolytic sources in the burning/burnt samples were identified. The lowest values of the sum of the 16 priority PAHs found in burning/burnt samples and the depletion LMW PAHs and greater abundance of HMW PAHs from the unburned coal waste material relatively to the burning/burnt material demonstrate the thermal transformation attributed to the burning process. The potential environmental impact associated with the coal waste piles are related with the release of petrogenic and pyrolytic PAHs in particulate and gaseous forms to soils, sediments, groundwater, surface water, and biodiversity.

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1. Introduction

The coalification process controls the chemical composition of coal, which varies considerably around the world [1,2]. Despite the numerous organic compounds that constitute coal, semi-volatile hydrocarbons represent part of those compounds, which include, among others, polycyclic aromatic hydrocarbons (PAHs).

Polycyclic aromatic hydrocarbons are known as a group of environmental organic pollutants that are harmful to the environment and to human health. The United States Environmental Protection Agency (US-EPA) has defined 16 PAHs as priority pollutants, due to their toxicity, mutagenic and carcinogenic properties. These compounds, with 2 to 6 condensed aromatic rings, are naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[123-cd]pyrene, dibenz[ah]anthracene, and benzo[ghi]perylene.

Environmental sources of PAHs associated with fossil fuels have been detailed in the literature, including natural and

anthropogenic sources [1]. Combustion of fossil fuels is considered as the major anthropogenic source of PAHs in the environment (pyrolytic source) while the natural source of PAHs is related to native PAHs in fossil fuels (petrogenic source), that has not been considered as a source of contamination [1]. However, the petrogenic source of PAHs in the environment can also result from anthropogenic activities, such as coal mining or oil spills. A review on the natural occurrence of PAHs in coals supported that PAHs in coal, arising from chemical conversion of organic matter, can also be a source of contamination [1]. Other studies [3,4] described PAHs concentrations and patterns in coals.

Petrogenic or native PAHs can be released to the environment during mining operations, transport, storage of coal and coal discard, among others, posing a risk to soils, sediments, groundwater, surface water, and biodiversity [1], and their physico-chemical properties largely determine the environmental behaviour [5]. These compounds are preferentially bounded to the particulate matter but some, such as naphthalene, fluorene, phenanthrene and anthracene, can be detected in water phases [6]. Their fate in the environment includes volatilization, photo-oxidation, chemical oxidation, adsorption in soil particles, leaching and microbial degradation [5].

Generally, PAHs with petrogenic origin have high amounts of naphthalene and phenanthrene [6]. However, the quantity and

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patterns of native PAHs in coals vary with rank since aromaticity increases with increasing coalification [1,7]. Low rank coals are characterized by low molecular weight PAHs (LMW PAHs) with 2 to 3 aromatic rings and, as coal rank increases, occurs a relative enhancement in the proportion of high molecular weight PAHs (HMW PAHs), with 4 to 6 aromatic rings [1]. However, other authors describe a predominance of HMW PAHs in low rank coals and a predominance of LMW PAHs in high rank coals [3,4]. The highest concentrations of PAHs are reported for high volatile bituminous coals, which may be explained by the increasing condensation of aromatic rings with increasing rank, when compared to low rank coals. However in high rank coals, such as anthracites, the concentrations of PAHs are much lower, which is attributed to the increase of PAHs with more than 6 aromatic rings at the expense of 2 to 6 ring PAHs due to rearrangement and fragmentation reactions [1,2].

Besides the petrogenic formation of HMW PAHs, especially with increasing rank, high temperature combustion produces pyrolytic PAHs with 4 to 6 rings [8]. Studies about the PAHs emissions from coal combustion for power generation supported that PAHs formation is highly dependent on the combustion temperature and oxygen ratios [9,10]. Thermodynamically, more stable PAHs are enriched in combustion products because thermodynamically unstable PAHs disappear during combustion [11]. Pyrolytic PAHs resulting from incomplete combustion are represented by a predominance of fluoranthene and pyrene as well as compounds with five and six aromatic rings [6].

Some recent studies refer to the occurrence and/or emission of PAHs associated with coal fires and highlight their environmental impact [2,12–21] and their health effects [13,21]. PAHs in burning coal waste piles may have various behaviours in the environment [18]: they can evaporate and enter the atmosphere, and some may re-precipitate in colder areas; they may also be retained or adsorbed within the waste material, or migrate within the waste piles where the more soluble compounds can be dissolved and migrate into the surrounding areas. Although poorly studied, the adverse effects of coal combustion in human health are related with the emission of toxic trace elements (arsenic, fluorine, selenium, mercury, among others), gases (carbon monoxide, carbon dioxide, other greenhouse gases, methane, sulfur dioxides, nitrous oxides, and organic compounds) and particulate matter, which may account for the occurrence of several health problems, such as respiratory, lung and skin diseases [13,21].

2. Case study and objectives

In the Douro Coalfield (NW of Portugal), the largest outcrop of terrestrial Carboniferous (Upper Pennsylvanian [Lower Stephanian C]) coal-bearing strata in Portugal is found [22–25], and the exploitation of anthracite A took place for many years (1795–1994).

One of the most significant environmental impacts caused by coal exploitation is the quantity of coal waste piles (more than 20) found all over the mining areas. Generally, the coal waste piles material consists of lithic fragments, normally carbonaceous shales and lithic arenites, with variable amounts of coal [20]. The Serrinha waste pile is the largest and resulted from the accumulation of overburdened material from the Pejão mining area, by simple discharge in a topographical depression. The burning of three of those waste piles, namely S. Pedro da Cova, Lomba and Midões, adds further to the environmental problems [20]. The S. Pedro da Cova waste pile is located very close to the oldest centre of mining activities in S. Pedro da Cova and near to a population centre and social infrastructures. This pile has an elongated form, occupying an area of approximately 28 000 m², with the burning process occurring only in the south slope and moving along it [20]. The sampling includes the collection of waste material, from burning or already

burnt zones and from unburned zones. The Lomba waste pile is located next to the south margin of the Douro River, on a private property and near a population centre. This waste pile occupies an area of approximately 7300 m² and burning has been moving along it. The sampling in the Lomba waste pile, included the collection of waste material, from burning or already burnt zones and from unburned zones. The Midões waste pile is very small when compared with the other burning waste piles (occupies approximately 200 m²) but it is located near a residential area. Samples of waste material from burning or already burnt in this coal waste pile were collected [20]. It is expected that the coal waste material contains PAHs from petrogenic origin due to their carbon content and, in addition, the burning waste piles can also contain PAHs of pyrolytic origin due to the burning process.

Previous studies on these coal waste piles dealt with petrographic, mineralogical and geochemical characterizations of the waste material, with the potential leaching of inorganic constituents of the waste material [20,26,27] and with gases emitted from gas vents in burning coal waste piles [20]. The analysis of gases exhibited a wide range of hydrocarbons, including aromatic and aliphatic hydrocarbons [20], which are known to have deleterious environmental and human health impacts [13,15]. It was also demonstrated that the burning coal waste piles may have reached combustion temperatures of about 1000 °C or even higher [20]. The study of carbon nanoparticles on the coal waste materials from Douro Coalfield recognized the formation of fullerenes and multiwalled carbon nanotubes during the thermal transformations caused by the burning process [28]. Fullerenes can retain some hazardous elements in their structure, and consequently this may have significant environmental and human health implications.

The objectives of this study are: (a) to identify and quantify the 16 priority PAHs in coal waste material from burning and non-burning coal waste piles; (b) to evaluate the petrogenic and pyrolytic sources of PAHs in the burning coal waste piles; (c) to assess the PAHs concentrations variation and its patterns due to the burning process in the coal waste piles; and (d) to contribute for the environmental impact assessment associated with the disposal of the mining wastes in coal waste piles, including those burning spontaneously.

3. Materials and analytical methodology

A total of 22 samples were collected from both non-burning coal waste pile (Serrinha) and burning coal waste piles (S. Pedro da Cova, Lomba, and Midões), which represent the major environmental concerns. The sampling was as follows: Lomba (5 samples from burning zones and 2 samples from unburned zones); S. Pedro da Cova (3 samples from burning zones and 3 samples from unburned zones); Midões (2 samples from burning zones); and Serrinha (6 samples from the non-burning coal waste pile). The coal waste material samples were collected near the surface, based on a sampling network representative, as possible, of the entire waste piles. In the laboratory the samples were dried, homogenized and quartered to obtain representative samples. The samples collection in the burning coal waste piles was highly dependent on the zones affected by combustion.

Each sample (50–100 g) was crushed to 1 mm, and extracted using an accelerated solvent extraction Dionex ASE 300. The extraction was carried out at temperature of 75 °C and pressure of 1500 psi, with dichloromethane as solvent. Activated copper was used to remove sulphur. After the solvent removal, the extracts were fractionated using a chromatographic silica gel column. The dried silica gel was activated and packaged in the glass column. Elution was performed using 6 mL of hexane to obtain the first fraction (aliphatic hydrocarbons), followed by 8 mL of

hexane/dichloromethane (50:50) to remove the second fraction (aromatic hydrocarbons). All extracts were collected, evaporated and weighed.

The aromatic hydrocarbon fractions from the coal waste material were analyzed using an Agilent gas chromatograph 7890A equipped with a 7693 auto sampler and coupled to a mass spectrometer detector 7000A system (GC/MS TripleQuad). The analyses were performed with a DB – 5 column (30 m × 0.25 mm i.d.) coated by 0.25 μm stationary phase film. These analyses were performed at the Laboratory of Palynofacies and Organic Facies of the Federal University of Rio de Janeiro.

The experimental conditions for all analyses were as follows: the carrier gas was He at 1.2 mL/min, in constant flow mode; the injector temperature was 290 °C; the GC oven temperature programme was: 40 °C (1 min) to 300 °C at 8 °C/min, held for 15 min. The mass spectrometer was operated in the electron impact ionization mode at 70 eV. Samples were analyzed in the selective ion monitoring (SIM) mode using *m/z* 128, 152, 154, 166, 178, 202, 212, 228, 252, 276, 278.

The PAHs compounds were identified using the NIST library search programme and the retention time. Quantitative analysis was done by preparing seven calibration standard solutions, from 0.01 μg/mL to 2 μg/mL, of a standard mixture containing the 16 priority PAHs. Blanks, duplicate samples and internal standard addition were employed for analytical assurance. Deuterated pyrene (D₁₀ – pyrene) was used as internal standard. The relative response factors of the calibration solutions were used to calculate the concentrations of the 16 priority PAHs in the samples.

4. Results and discussion

4.1. PAHs in coal waste material

The GC–MS analyses were performed on coal waste samples from both non-burning coal waste pile (Serrinha) and burning coal waste piles (Lomba, S. Pedro da Cova and Midões). In the burning coal waste piles, two zones were considered: burning/burnt and unburned zones. The concentrations of the 16 priority PAHs of each studied coal waste material sample are presented in Table 1, together with the sum of the 16 priority PAHs.

The concentrations of PAHs show some similarity among the studied samples, except for sample M68 which presents much higher concentrations of the high molecular weight PAHs (HMW PAHs). On the other hand, the concentrations of the low molecular weight PAHs (LMW PAHs) in sample M68 are similar to the concentrations in the other samples.

The most abundant PAH in the samples is phenanthrene, followed by minor proportions of fluoranthene and pyrene. Naphthalene was not detected in almost all samples and benzo[k]fluoranthene was detected in few samples (S18, L71, L74, L69, L73, and M68). Generally, PAHs from petrogenic origin present high amounts of naphthalene and phenanthrene [6], which is in accordance with the phenanthrene concentrations detected in the studied samples. The absence of naphthalene could be attributed to the high rank of the coal present in the studied materials [1,2] or to the volatilization of this compound during extraction procedures.

The sum of the 16 PAHs ranges between 2.63 ng/g and 10.71 ng/g in the samples from Serrinha waste pile, between 2.87 ng/g and 15.45 ng/g in Lomba, and between 3.82 ng/g and 15.48 ng/g in S. Pedro da Cova. In the Midões waste pile 4.47 ng/g and 70.97 ng/g were detected in samples M11 and M68, respectively, which differ greatly as previously mentioned for sample M68. The variable sum of the 16 PAHs in the studied samples depends on the carbon content of the samples, which, in this case, varies between 1.2 wt.% and 34.4 wt.%.

4.2. PAHs behaviour and patterns attributed to combustion in burning coal waste piles

Generally, samples from the burning/burnt zones of the Lomba and S. Pedro da Cova reported the lowest values for the sum of the 16 priority PAHs, when compared with those of the unburned zones (Table 1). The mean value of the sum of the 16 PAHs is 11.6 ng/g in the unburned waste material from Lomba and S. Pedro da Cova and 6.9 ng/g in burning/burnt material from Lomba and S. Pedro da Cova. The lowest values of the mean of the sum of PAHs in the burning/burnt zones when compared with those of the unburned zones are probably due to the volatilization of the less stable PAHs during the heating process [1,2,11].

On the basis of the number of aromatic rings, PAHs are classified as LMW PAHs containing 2 to 3 rings and HMW PAHs with 4 to 6 rings. The sum of the relative percentages of LMW PAHs and HMW PAHs of samples collected in the burning coal waste piles were calculated and the results are presented in Table 2, which demonstrates the predominance of LMW PAHs comparatively with the HMW PAHs in unburned waste material. However, in samples collected from burning/burnt zones, the percentage of LMW PAHs tends to decrease and that of the HMW PAHs to increase. This indicates the formation of pyrolytic PAHs with 4 to 6 rings derived from the thermal decomposition of the native PAHs [8].

Fig. 1 illustrates the mean relative percentages of each of the 16 priority PAHs in unburned and in burning/burnt coal waste materials from the studied burning coal waste piles. Despite the differences in the proportions of the LMW PAHs and the HMW PAHs, Fig. 1 illustrates a similar pattern between unburned and burning/burnt samples, i.e., the most abundant is phenanthrene followed by fluoranthene and pyrene, with the other PAHs being present in lower concentrations. Fig. 1 shows a predominance of LMW PAHs, especially phenanthrene, in the unburned coal waste material relatively to the burning/burnt coal waste material. On the other hand, the HMW PAHs manifest high proportions in the burning/burnt coal waste material, indicating the formation of pyrolytic PAHs with 4 to 6 rings derived from the thermal decomposition of the native PAHs, which is in accordance with what was mentioned above. Recent studies from other authors [2] about PAHs concentrations and patterns arising from thermal transformations of organic matter derived from natural coal fires also reported the decrease in LMW PAHs and the increase of HMW PAHs due to thermal transformation.

Several authors use PAHs ratios for fossil fuels source assignments in environmental studies [6,11,29,30]. Some ratios of selected PAHs concentrations allow differentiation between petrogenic and pyrolytic emission sources of PAHs. Because of their differing physico-chemical properties, phenanthrene and anthracene behave differently in the environment [5,29]. Since phenanthrene is more thermodynamically stable than anthracene, the PHE/ANT ratio could give valuable information on the PAHs origin. The ratios calculated for the studied samples are presented in Table 2 – values greater than 15 indicate a petrogenic source of PAHs whereas those less than 10 indicate a pyrolytic source.

In general, samples from unburned zones of Lomba, S. Pedro da Cova waste piles presented values of PHE/ANT higher than 15 and a mean value of 19.1, which indicate the petrogenic source of the PAHs. Some of the samples from burning/burnt zones presented values below 10, indicating a pyrolytic source for the PAHs. However, some samples from burning/burnt zones present values greater than 10 but less than 15. The mean value of PHE/ANT ratio in burning/burnt samples is 12.8, which could indicate a mixture of petrogenic and pyrolytic PAHs associated with the burning waste piles. Even considering the PHE/ANT ratios it was noticed that PAHs from pyrolytic contribution seemed to be more intense in some samples associated with burning coal wastes (PHE/ANT < 10). This

Table 1
Concentrations (ng/g on dry basis) of the 16 priority PAHs in the samples and sum of the 16 priority PAHs.

16 Priority PAHs			NAP	ACFT	ACE	FLUO	PHE	ANT	FLT	PYR	BaA	CRY	BbF	BkF	BaP	InP	DaA	BgP	16 PAHs
No. of aromatic rings			2	2	2	2	3	3	4	4	4	4	4	4	5	5	5	6	
Molecular weight			LMW PAHs							HMW PAHs									
Serrinha waste pile (S)	UB	S4	n.d.	0.09	0.43	0.33	3.88	0.25	0.84	0.65	0.22	0.12	0.20	n.d.	0.16	0.16	0.03	0.04	7.41
		S8	n.d.	0.16	0.04	n.d.	n.d.	0.26	0.30	n.d.	0.44	0.25	0.34	n.d.	0.32	0.35	0.08	0.08	2.63
		S15	n.d.	0.09	0.02	n.d.	3.72	0.15	0.06	0.33	0.25	0.11	0.20	n.d.	0.17	0.18	0.04	0.05	5.39
		S16	n.d.	0.24	0.10	1.86	5.47	0.21	0.63	n.d.	0.22	0.16	0.18	n.d.	0.15	0.16	0.04	0.05	9.46
		S18	n.d.	0.13	0.04	0.24	4.74	0.36	1.34	1.03	0.44	0.30	0.73	0.31	0.54	0.33	0.05	0.10	10.67
		S20	n.d.	0.07	0.02	0.46	6.70	0.21	1.50	0.88	0.21	0.16	0.17	n.d.	0.13	0.14	0.03	0.04	10.71
Lomba waste pile (L)	UB	S21	n.d.	0.11	0.03	0.10	3.34	0.21	0.47	0.33	0.31	0.15	0.19	n.d.	0.20	0.24	0.06	0.07	5.80
		L71	0.17	0.15	0.88	0.63	8.23	0.36	1.61	1.29	0.27	0.23	0.22	0.21	0.37	0.19	0.05	0.05	14.89
		L74	n.d.	0.17	0.02	0.04	3.19	0.30	1.62	1.04	0.36	0.38	0.34	0.13	0.16	0.21	0.05	0.08	8.08
	B	L68	n.d.	0.10	0.02	0.10	1.68	0.18	0.32	0.17	0.26	0.09	0.18	n.d.	0.19	0.20	0.04	0.05	3.57
		L69	n.d.	0.15	0.02	0.13	4.57	0.31	3.54	2.89	0.69	1.13	0.66	0.72	0.28	0.21	0.04	0.09	15.45
		L70	n.d.	0.08	0.02	0.06	1.18	0.15	0.26	0.14	0.24	0.11	0.15	n.d.	0.16	0.20	0.05	0.06	2.87
S. Pedro da Cova waste pile (SP)	UB	L72	n.d.	0.10	0.07	0.42	3.12	0.24	0.66	0.46	0.25	0.13	0.22	n.d.	0.17	0.18	0.04	0.05	6.10
		L73	n.d.	0.08	0.02	0.09	2.79	0.20	0.39	0.23	0.36	0.23	0.29	0.13	0.27	0.30	0.15	0.18	5.71
		SP10	n.d.	0.08	0.05	0.94	9.78	0.35	1.38	1.73	0.20	0.05	0.24	n.d.	0.22	0.21	0.04	0.22	15.48
	B	SP37	n.d.	0.12	0.03	0.07	5.49	0.27	1.17	0.72	0.33	0.19	0.26	n.d.	0.23	0.26	0.06	0.06	9.26
		SP38	n.d.	0.21	0.06	0.89	6.53	0.47	0.60	0.59	0.25	0.10	0.16	n.d.	0.18	0.20	0.05	0.05	10.34
		SP30	n.d.	0.09	0.09	0.26	1.71	0.18	0.33	0.20	0.22	0.06	0.23	n.d.	0.20	0.17	0.04	0.04	3.82
Midões waste pile (M)	B	SP33	n.d.	0.11	0.03	0.85	8.36	0.46	1.14	0.96	0.22	0.15	0.18	n.d.	0.14	0.16	0.03	0.05	12.84
		SP34	n.d.	0.07	0.02	0.27	2.91	0.18	0.19	0.07	0.18	0.05	0.13	n.d.	0.13	0.15	0.03	0.03	4.42
		M11	n.d.	0.11	0.03	0.31	2.03	0.24	0.35	0.24	0.29	0.09	0.22	n.d.	0.22	0.23	0.05	0.06	4.47
		M68	n.d.	0.11	0.03	0.34	9.22	0.54	13.76	10.26	4.36	5.78	7.49	11.56	3.13	2.05	0.45	1.88	70.97

NAP, naphthalene; ACFT, acenaphthylene; ACE, acenaphthene; FLUO, fluorene; PHE, phenanthrene; ANT, anthracene; FLT, fluoranthene; PYR, pyrene; BaA, benzo[a]anthracene; CRY, chrysene; BbF, benzo[b]fluoranthene; BkF, benzo[k]fluoranthene; BaP, benzo[a]pyrene; InP, indeno[123-cd]pyrene; DaA, dibenz[ah]anthracene; BgP, benzo[ghi]perylene; LMW PAHs, low molecular weight PAHs; HMW PAHs, high molecular weight PAHs; UB, samples from unburned zones; B, samples from burning/burnt zones; n.d., not detected.

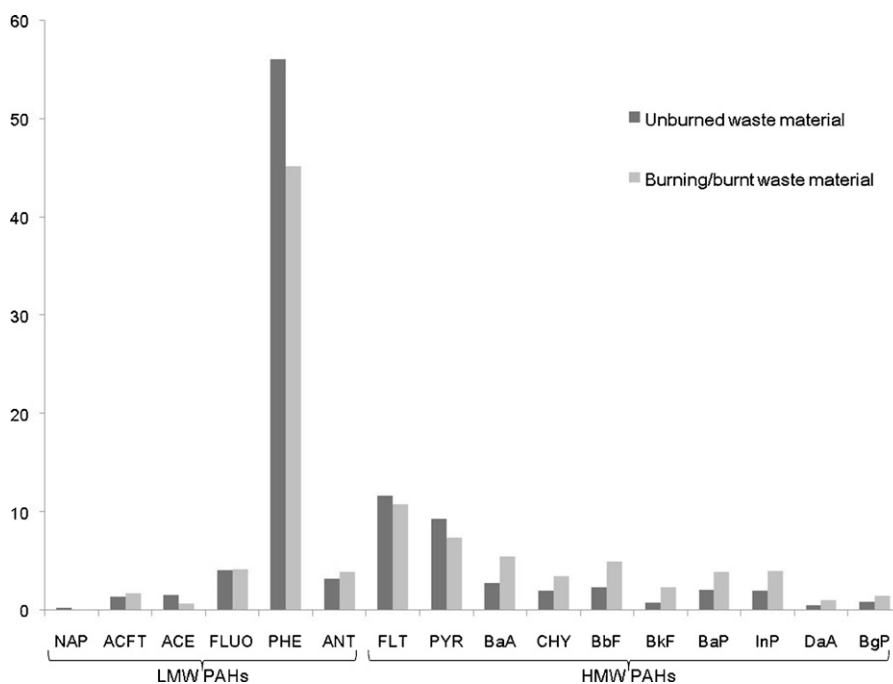


Fig. 1. Mean relative percentages of the 16 priority PAHs in unburned coal waste material (L71, L74, SP10, SP37, and SP38) and burning/burnt coal waste material (L68, L69, L70, L71, L73, SP30, SP33, SP34, M11, and M68). Abbreviations as described in Table 1.

Table 2

Relative percentages of LMW PAHs and HMW PAHs and PHE/ANT ratio of samples from burning coal waste piles.

		% LMW PAHs	% HMW PAHs	PHE/ANT
Unburned waste material	L 71	70.0	30.0	23.1
	L 74	46.1	53.9	10.5
	SP 10	72.4	27.6	28.0
	SP 37	64.5	35.5	20.2
	SP 38	78.9	21.1	13.9
	Mean	66.4	33.6	19.1
Burning/burnt waste material	L 68	58.0	42.0	9.5
	L 69	33.5	66.5	14.7
	L 70	52.3	47.7	7.7
	L 72	64.8	35.2	13.2
	L 73	55.8	44.2	13.9
	SP 30	61.1	38.9	9.3
	SP 33	76.3	23.7	18.3
	SP 34	78.0	22.0	15.8
	M 11	60.9	39.1	8.5
	M 68	14.4	85.6	17.1
	Mean	55.5	44.5	12.8

LMW PAHs, low molecular weight PAHs; HMW PAHs, high molecular weight PAHs; PHE/ANT, phenanthrene concentration/anthracene concentration ratio; L, Lomba waste pile; SP, S. Pedro da Cova waste pile; M, Midões waste pile.

could mean that samples were differently affected by burning process in the coal waste piles. Previous studies also demonstrated that the burning coal waste piles experienced different burning intensities [20].

5. Conclusions

The concentration of the 16 priority PAHs was determined in the organic fraction of the coal waste material from both non-burning and burning/burnt coal waste piles from the Douro Coalfield.

The studied samples present some similarity in PAHs concentrations. Phenanthrene is the most abundant PAH followed by fluoranthene and pyrene. The lowest values of the sum of the 16 priority PAHs found in burning/burnt samples point toward the thermal alteration of the PAHs.

Depletion of LMW PAHs and greater abundance of HMW PAHs from the unburned coal waste material relatively to the burning/burnt material also demonstrate the thermal transformation attributed to the burning process.

The ratio PHE/ANT was useful in the identification of pyrolytic source of PAHs in the burning coal waste piles. The results show a petrogenic contribution of PAHs in unburned samples and a mixture of PAHs from petrogenic and pyrolytic sources in the burning/burnt samples. The variable values of PHE/ANT in some of burning/burnt samples could be attributed to the variable burning intensity in the coal waste piles.

The potential environmental impact associated with these coal waste piles are related with the native PAHs in the coal waste material. The PAHs may be released to soils, sediments, groundwater, surface waters, and biodiversity. The burning of some coal waste piles has added further to the environment and even human health impacts given that PAHs may also be emitted to the atmosphere in particulate and gaseous forms.

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