Water Quality Concerns Due to Forest Fires: Polycyclic Aromatic Hydrocarbons (PAH) Contamination of Groundwater From Mountain Areas

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WATER QUALITY CONCERNS DUE TO FOREST FIRES: POLYCYCLIC AROMATIC HYDROCARBONS (PAH) CONTAMINATION OF GROUNDWATER FROM MOUNTAIN AREAS

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Water quality alterations due to forest fires may considerably affect aquatic organisms and water resources. These impacts are cumulative as a result of pollutants mobilized from fires, chemicals used to fight fire, and postfire responses. Few studies have examined post-fire transport into water resources of trace elements, including the polycyclic aromatic hydrocarbons (PAH), which are organic pollutants produced during combustion and are considered carcinogenic and harmful to humans. PAH are also known to adversely affect survival, growth, and reproduction of many aquatic species. This study assessed the effects of forest wildfires on groundwater from two mountain regions located in protected areas from north and central Portugal. Two campaigns to collect water samples were performed in order to measure PAH levels. Fifteen of 16 studied PAH were found in groundwater samples collected at burned areas, most of them at concentrations significantly higher than those found in control regions, indicating aquifer contamination. The total sum of PAH in burned areas ranged from 23.1to 95.1 ng/L with a median of 62.9 ng/L, which is one- to sixfold higher than the average level measured in controls (16.2 ng/L). In addition, in control samples, the levels of light PAH with two to four rings were at higher levels than heavy PAH with five or six rings, thus showing a different profile between control and burned sites. The contribution of wildfires to groundwater contamination by PAH was demonstrated, enabling a reliable assessment of the impacts on water quality and preparation of scientifically based decision criteria for postfire forest management practices.

Wildfires, both natural and synthetic, are a major international concern with a tremendous impact on environment, the economy, tourism, society, and human health.

Portugal faces the risk of wildfires every summer, and the situation is getting worse due to heat waves, dry weather, and erratic rains. In 2013, seven firefighters died, dozens were injured, and hundreds of individuals were evacuated and severely affected socially and economically. In response to the risks of forest fire, it is therefore important to have integrated strategies and policies capable for forest fire prevention and remediation (Forest Europe Liaison Unit Oslo, 2010; European Forest Fire Information System [EFFIS], 2013).

Natural waters are severely affected by wildfires. Erosion, ash deposition, soil hydrophobicity, landslides, and flooding are some of the biggest concerns after a fire that alters the quality of water. Independent of fire type and intensity, the combustion process generates vast amounts of carbon dioxide and several groups of pollutants, including

dioxins, dibenzofurans, and polycyclic aromatic hydrocarbons (PAH) (Austin et al, 2001; Lemieux, 2004). Due to their potential adverse effects on humans and wildlife, PAH are registered on European and American lists of priority pollutants that need to be monitored in the environment (U.S. Environmental Protection Agency [EPA], 2008). There is concern regarding PAH relating to toxicity, carcinogenicity, environmental long-term persistence, widespread occurrence, long-range transportation, and tendency to bioaccumulate (Smith et al., 2011a; International Agency for Research on Cancer [IARC] and World Health Organization [WHO], 2010), which resulted in classification as persistent organic pollutants (POP). It is also important to consider that in natural waters, PAH may undergo various transformations such as volatilization and photochemical degradation; these physicochemical properties are responsible for different interactions with suspended matter, sediments, and biota.

Regarding water quality, PAH were firstly considered priority hazardous substances by Decision No. 2455/2001/EC of the European Parliament and of the Council of 20 November 2001, which became Annex X of the Water Framework Directive (2000/60/EC). This list was replaced by Annex II of the Directive on Environmental Quality Standards (Directive 2008/105/EC), also known as the Priority Substances Directive, subsequently reviewed by the European Commission (EC) in 2012 (COM(2011) 876 final). The European Commission proposal concerned evaluation of the list of priority substances in the field of water policy, where chemicals were identified among those presenting a significant risk to or via the aquatic environment at European Union (EU) level.

In environmental water analysis, one of the most critical steps involved in determination of these contaminants is sample pretreatment, which needs to include an accurate procedure for extraction, isolation, and concentration of the analytes. Currently, there are several "environmentally friendly" extraction procedures available, but solid-phase extraction (SPE) continues to be one of the

most reliable methodologies, allowing for high enrichment factors. Therefore, SPE coupled with gas chromatography/mass spectrometry (GC/MS) is commonly accepted as one of the most powerful techniques for organic pollutants analysis, even in the nanogram (ng) range (Alder et al., 2006; Viglino et al, 2008). In this study, a multiresidue method for detection and quantification of trace levels of PAH in water matrices was optimized and validated following international recommendations (International Conference on Harmonisation [ICH], 1995, 1997, 2005; Food and Drug Administration [FDA], 2001; National Committee for Clinical Laboratory Standards [NCCLS], 2002; Clinical and Laboratory Standards Institute [CLSI], 2006). Unequivocal analytical data require a specific set of validation criteria and method performance verification to ensure international acceptance of analytical results. Matrix-standard calibration solutions were used to avoid matrix-induced chromatographic response enhancement. It is noteworthy that verified heteroscedasticity was supplanted by a weighted least-squares linear regression model application (WLSLR) (Mansilha et al., 2010; Miller and Miller, 2005) that provides unbiased estimative for prediction, calibration, and optimization when standard deviations of data random errors are not constant across all levels of the explanatory variables.

Several studies demonstrated the influence of forest fires on air quality (Okuda et al., 2002), sediments and soil (Kim et al., 2011; Vergnoux et al., 2011), and riverine waters (Olivella et al, 2006), but, to the best of our knowledge, there are few investigations on the impact of extensive forest fires on groundwater contamination by PAH, as well as on the influence of climatic conditions and time elapsed since the last fire.

The aim of this study was to determine levels of PAH in groundwater samples from two sectors located in mountain regions of two Portuguese protected areas where forest wildfires exerted a devastative effect (Figures 1 and 2): Serra da Estrela (Central Portugal) and Serra do Gerês (North Portugal). Unburned areas were also selected for water sampling and considered as controls.
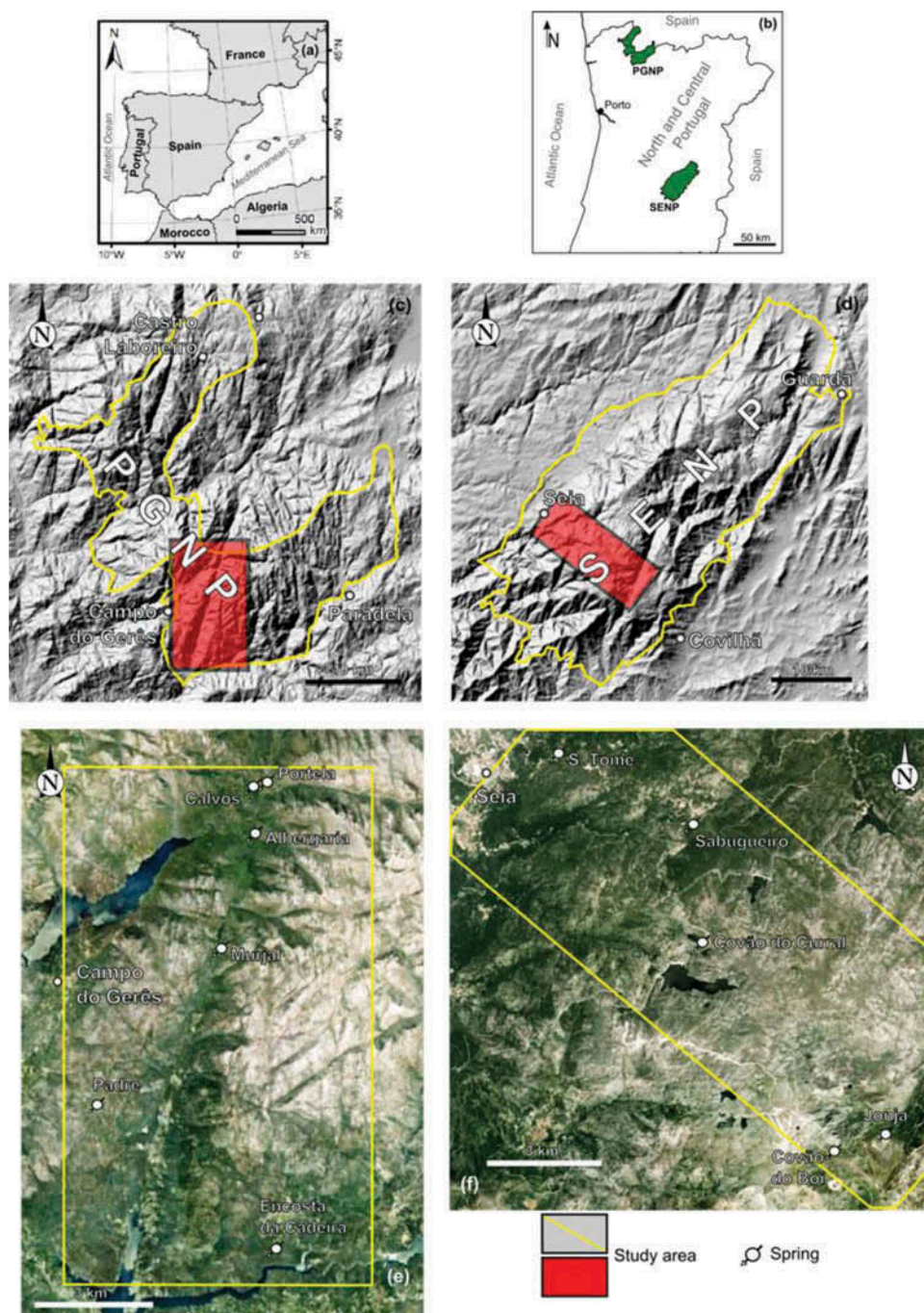
FIGURE 1. Location of the PGNP and SENP protected areas (a, b, c, and d). Location of the studied sectors (c, d, e, and f). Location of the water points (e and f). (Satellite images from Google Earth.)

MATERIAL AND METHODS

Chemicals and Reagents

PAH calibration mix (naphthalene, Nap; acenaphthylene, Acy; acenaphthene, Ace; fluorene, Flu; phenanthrene, Phe; anthracene, Ant; fluoranthene, Flt; pyrene, Pyr; benz[a]anthracene, BaA; chrysene, Chr; benzo[b]fluoranthene, BbF; benzo[k]fluoranthene (BkF); benzo[a]pyrene, BaP; dibenz[a,h]anthracene, DahA; benzo[ghi]perylene, BghiP; and indeno[1,2,3-cd]pyrene,
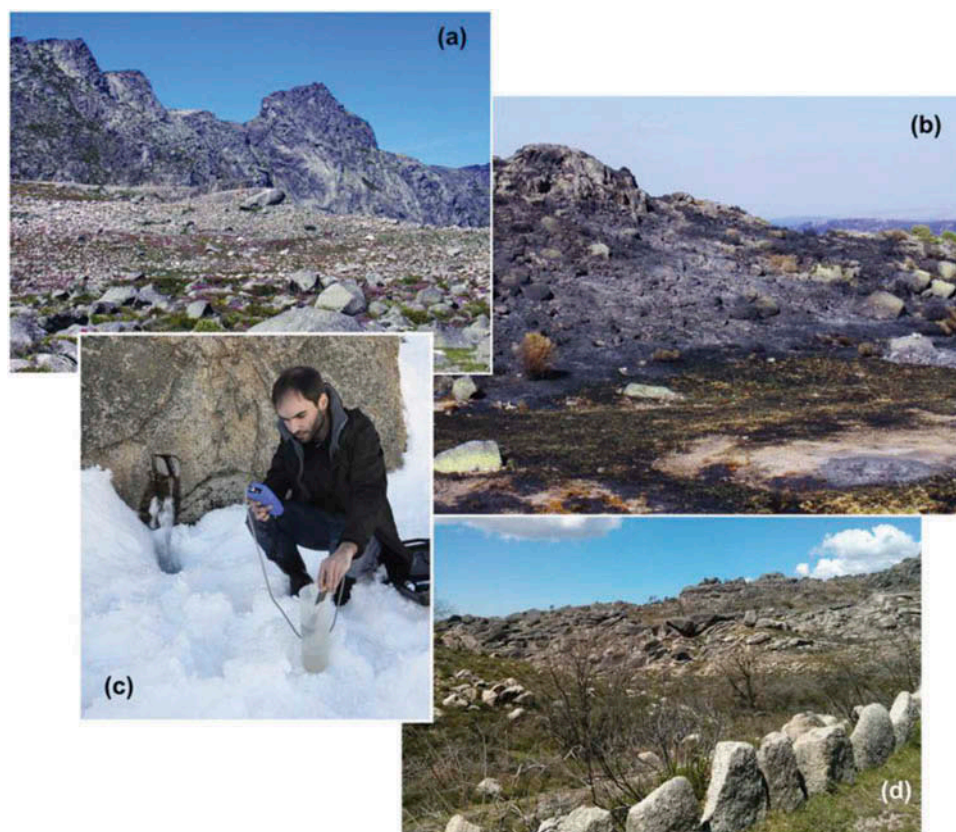
FIGURE 2. Some aspects from the study sites: landscape from Serra da Estrela showing loss of vegetation as a consequence of recurrent wildfires (a); recently burned slope at Serra da Estrela (b); field measurements at Covão do Boi spring (c); vegetation cover recovery in a burned area at Serra do Gerês (d).

**TABLE 1.** Quantitation and Identification Ions for the GC-MS Analyses of Selected PAHs

	RT (min)	Quantitation ions (m/z)	Identification ions (m/z)
Naphthalene (Nap)	5.293	128	127; 128; 129
Acenaphthylene (Acy)	6.933	152	151; 152; 153; 154
Acenaphthene (Ace)	7.153	154	151; 152; 153; 154
Fluorene (Flu)	7.973	166	165; 166; 167
Phenanthrene (Phe)	9.927	178	176; 178; 179
Anthracene (Ant)	10.033	178	176; 178; 179
Fluoranthene (Flt)	12.220	202	101; 202; 203
Pyrene (Pyr)	12.615	202	101; 202; 203
Benz[a]anthracene (BaA)	14.733	228	226; 228; 229
Chrysene (Chr)	14.790	228	226; 228; 229
Benzo[b]fluoranthene (BbF)	16.716	252	126; 252; 253
Benzo[k]fluoranthene (BkF)	16.784	252	126; 252; 253
Benzo[a]pyrene (BaP)	17.457	252	126; 252; 253
Indeno[1,2,3-cd]pyrene (Ind)	19.886	276	138; 139; 276; 277; 278
Dibenz[a,h]anthracene (DahA)	19.986	278	138; 139; 276; 277; 278
Benzo[ghi]perylene (BghiP)	20.493	276	138; 139; 276; 277; 278

Note. RT, retention time.

TABLE 2. Method Validation Data With Calibration Parameters

	b	a	r	$\sum$%ER	LD (ng/L)	LQ (ng/L)
Naphthalene (Nap)	710.6	1356.0	0.9998	12.2	0.9	3.1
Acenaphthylene (Acy)	1337.6	2327.5	0.9992	15.8	2.9	9.6
Acenaphthene (Ace)	903.2	1048.2	0.9999	4.7	1.1	3.7
Fluorene (Flu)	1130.0	1397.1	0.9999	4.5	1.0	3.3
Phenanthrene (Phe)	1978.2	48683.5	0.9998	6.7	1.6	5.3
Anthracene (Ant)	1588.2	−3195.9	0.9999	4.5	1.0	3.4
Fluoranthene (Flt)	2332.2	7156.2	0.9997	9.9	2.1	6.9
Pyrene (Pyr)	2464.5	4428.4	0.9998	6.9	4.2	13.9
Benz[a]anthracene (BaA)	1306.5	−6476.7	0.9999	4.4	0.9	2.9
Chrysene (Chr)	1472.9	665.8	0.9997	6.1	1.0	3.4
Benzo[b]fluoranthene (BbF)	1091.3	−5893.0	0.9997	9.8	1.8	5.9
Benzo[k]fluoranthene (BkF)	1121.4	−2839.0	0.9998	5.0	0.8	2.7
Benzo[a]pyrene (BaP)	1204.7	−5774.1	0.9999	8.5	1.1	3.6
Dibenz[a,h]anthracene (DahA)	834.0	−6032.8	0.9998	8.8	1.5	5.0
Benzo[ghi]perylene (BghiP)	960.9	−7693.7	0.9999	8.0	0.7	2.3
Indeno[1,2,3-cd]pyrene (Ind)	819.0	−5047.0	0.9997	12.8	1.6	5.3

Note. b, Slope; *a*, weighted intercept; *r*, weighted correlation coefficient; $\sum$%ER, sum of relative errors; *LOD*, limit of detection of the method; *LOQ*, limit of quantification of the method.
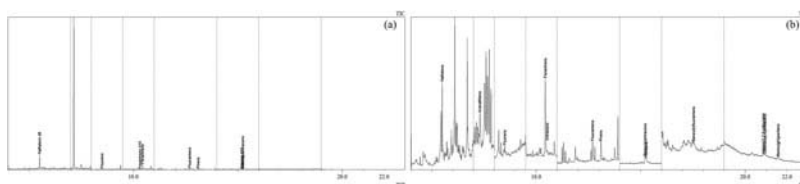
FIGURE 3. Chromatographic profiles of two samples collected in Serra da Estrela, in an unburned area (a) and in a burned one (b).
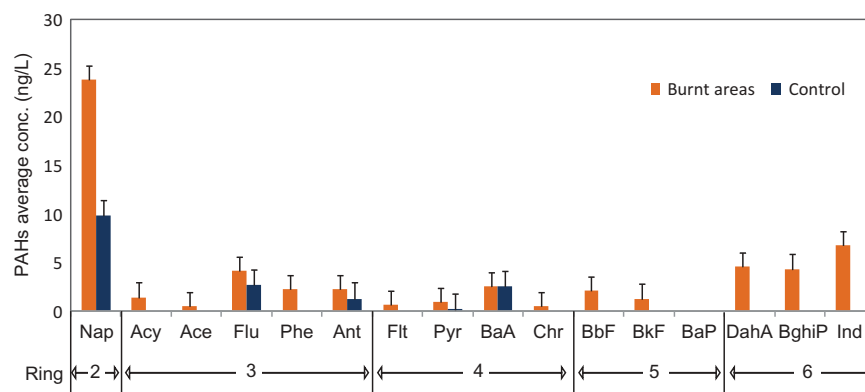
FIGURE 4. Average concentrations of PAH (individual fractions) in the burned ($n = 9$) and unburned (control) areas ($n = 2$).

Ind) was purchased from Sigma-Aldrich (Steinheim, Germany) (Figure 3). Methanol, dichloromethane, and acetonitrile were organic trace analysis grade SupraSolv and were obtained from Merck (Darmstadt, Germany). Ultrapure water was highly purified by a Milli-Q gradient system (18.2 mΩ-cm) from Millipore (Milford, MA).

For calibration purposes, a stock standard solution was prepared in acetonitrile by dilution of PAH mixture to a concentration of 1000 μg/L. Matrix-standard calibration solutions

(residue-free matrix spiked with standards), at concentration levels ranging from 0.01 μg/L to 0.1 μg/L per compound, were prepared by spiking 500 ml water with different volumes of the 1000 μg/L stock solution just before extraction.

SPE-GC/MS Conditions

SPE was conducted in an SPE vacuum manifold system using Strata PAH cartridges from Phenomenex (Torrance, CA). SPE conditions were as follows: (a) conditioning step, by the sequential addition of 10 ml dichloromethane, 10 ml methanol, and 20 ml Milli-Q water at a flow rate of 1 ml/min; (b) loading step, by passing the sample/standard through the cartridges at a flow rate of 5 ml/min; (c) washing step, by rinsing the cartridge with 3 ml water/methanol 1:1 and dried by vacuum pressure during approximately 30 s; and (d) elution performed with 2×3 ml dichloromethane, at a flow of 1 ml/min. After elution, the organic phase was transferred to a new tube, evaporated to dryness in a rotative evaporator (Buchi/Brinkman Rotavapor RE-111 and Water Bath B-461), and reconstituted within acetonitrile to a final volume of 500 μl.

Chromatographic analyses were carried out in a Shimadzu GCMS-QP2010 gas chromatograph mass spectrometer equipped with an auto injector AOC-5000. Injections (1 μl) were conducted in the splitless mode with a 1-min purge-off time and injector temperature set at 280°C. Helium (99.9999%) at a constant flow rate of 1.5 ml/min was used as the carrier gas.

Samples were analyzed using a fused-silica capillary column, Zebron ZB-5MS (30 m × 0.25 mm ID, 0.25 μm film thickness), with the following oven program temperature: initial temperature 70°C (held for 2 min), increased by 25°C/min to 180°C (held for 2 min), increased by 15°C/min to 280°C (held for 2 min), and increased again by 10°C/min to 300°C, and held at this temperature for 5 min.

Positive fragment ions (m/z, ions mass/charge ratio) were analyzed over 45–500 m/z mass range in full scan mode and in selected-ion monitoring (SIM) mode.

Instrument control and mass spectrometry data were managed by a personal computer running the LabSolutions GCMS software (2.50 SU3 version). The optimized methodology was applied for environmental water samples analysis.

Samples Collection

Two campaigns to collect water samples were performed in order to measure PAH concentrations with time. The studied sectors are located in the so-called Iberian Massif (Farias et al., 1987, Ribeiro et al., 2007): Serra do Gerês sector is located in the Galicia Trás-os-Montes Zone and Serra da Estrela sector is located in the Central-Iberian Zone. In both cases, geological setting is dominated by occurrence of variscan granitic rocks, with minor areas corresponding to metasedimentary rocks and sedimentary cover (Ferreira et al., 1987; Dias et al., 1998).

The altitude of the Serra do Gerês sector varies from around 400 m above sea level (a.s.l.) to 1200 m a.s.l. According to the Köppen–Geiger climate classification, this region has a Csb climate (warm temperate, with dry and warm summers), the same as northwestern Iberia (AEMET-IM, 2011). Information regarding air temperature and precipitation is scarce. The annual precipitation at the Gerês meteorological station (370 m a.s.l.) is around 2994 mm; at the Albergaria meteorological station (800 m a.s.l.) it reaches 3300 mm, while in the upper areas of the mountain it may reach 3500 mm/yr (Daveau et al., 1977; Mendes and Bettencourt, 1980; INMG, 1990). The mean annual air temperature at the Gerês station is 14°C; in August the mean is 21°C and in January the mean is 8°C (Mendes and Bettencourt, 1980). Daveau et al. (1985) estimated that in the upper area of the mountain, the mean minimal air temperature was under 1°C during the coldest month. For the same area, the mean maximal air temperature of the warmest month was less than 23°C.

The altitude of the Serra da Estrela sector ranges from 500 m a.s.l. to 1993 m a.s.l.
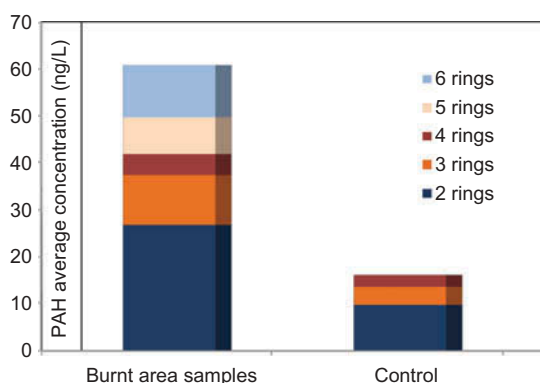
FIGURE 5. Average PHA profiles of the samples collected in burned and control areas according to their structural composition (number of benzene rings).
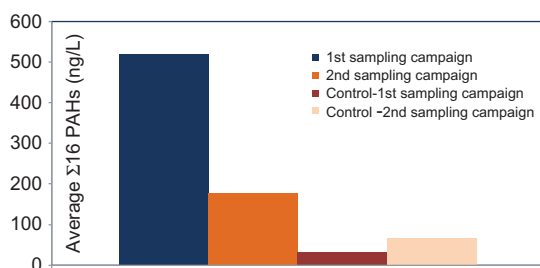

FIGURE 6. Temporal variations on PAHs concentrations (average Σ16 PAHs).

According to the Köppen–Geiger climate classification, the Serra da Estrela region has a Csb climate (warm temperate, with dry and warm summers; AEMET-IM, 2011). Yet the southern part of the mountain has a climate influence

of Csa subtype (warm temperate, with dry and hot summers). Mean annual precipitation is approximately 2500 mm in the uppermost areas, and mean annual air temperatures are below 7°C in most of the plateau area (Daveau et al., 1997, Espinha Marques et al., 2011). Mean annual air temperature may be as low as 4°C near the summit.

The sampling points (Figure 1) consisted of springs from water-table aquifers from areas affected by wildfires (5 in Serra do Gerês and 4 in Serra da Estrela)—hence the interest in determining the content of the 16 PAH listed by the U.S. EPA as priority pollutants. Samples from unburned areas (Murjal Spring and Covão do Boi Spring) were also collected and used as control. The criteria to select the groundwater points were that (i) water needs to flow throughout the year and (ii) springs need to be located far from industrial or residential areas and upstream from roads, in order to avoid PAH contamination from road traffic.

Sampling took place in spring 2011 in Serra da Estrela and in summer 2012 in Serra do Gerês. A second sampling campaign was performed with a year interval, after intense precipitation conditions. Water samples were collected in glass amber bottles (Figure 2) and refrigerated at 4°C until analysis. Water pH, electrical conductivity, and temperature were measured in situ at the moment of sampling.
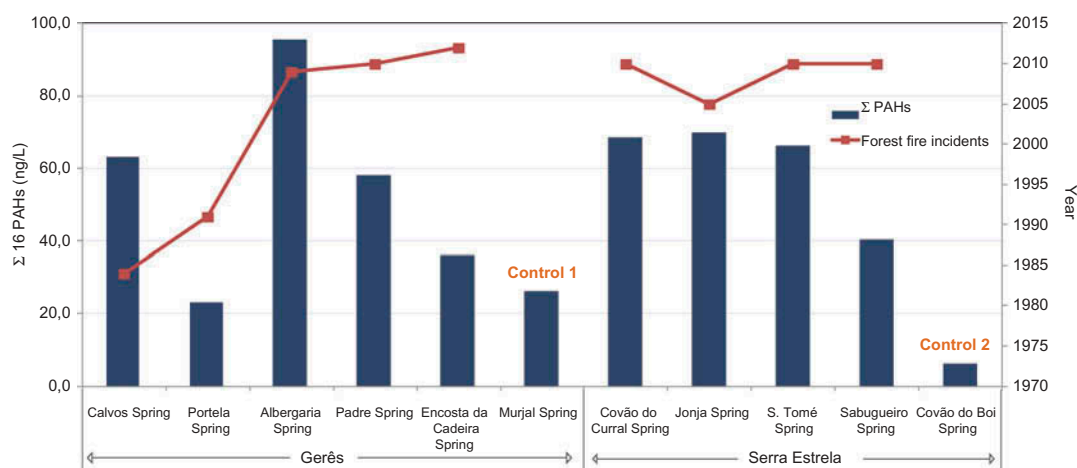

FIGURE 7. Sum of PAHs concentrations in samples collected at Serra da Estrela and Serra do Gerês and time elapsed since the last fire.

RESULTS AND DISCUSSION

Optimization and validation of the methodology for PAH analysis were conducted and results presented were according to method performance acceptability criteria. Analytes were identified by both their chromatographic characteristics, as retention time (RT), and through their specific fragmentation. Programs were developed in the SIM mode based on detection of selected ions for each analyte (Table 1). A multiresidue method was selected to enable simultaneous analysis of several compounds.

Specificity and selectivity were evaluated by comparing the chromatograms of matrix-blank samples with an aqueous solution of analytes at concentrations near the limits of quantification (LOQ). No significant interferences were detected at RT of the analyzed PAH. Selectivity was also assessed by comparison of the analytes mass spectra with spectra from libraries. Calibration parameters are presented in Table 2.

Fifteen of the 16 PAH were found in groundwater samples collected in burned areas, most of them at concentrations significantly higher than those present in control areas, which indicates aquifer contamination (Figure 3). Average PAH concentrations (individual fractions) are shown in Figure 4. As noted, the PAH Nap, Flu, Ant, BaA, DahA, BghiP, and Ind appeared to be the predominant pollutants produced.

Regarding the total sum of PAH ($\Sigma16$ PAH) in burned areas, values ranged from 23.1 to 95.1 ng/L, with a median of 62.9 ng/L, values that were one- to sixfold higher than the average level measured in controls (16.2 ng/L). In addition in control samples, the levels of light PAH with two to four rings were markedly higher than for heavy PAHs with five or six rings, with Nap the most abundant compound (60% of the total concentrations). In forest fires samples, Nap contributed 41%, while DahA, BghiP, and Ind contributed approximately 27%, thus showing a different profile in chemicals between burned and control locations (Figure 5).

Temporal variations on PAH concentration were also evaluated. A second campaign took place 1 year after the first one after heavy rainfalls that occurred 2–3 months earlier and results are shown in Figure 6. The decline of PAH with time, ranging from 10 to 30.5 ng/L, may be attributed to a dilution effect rather than biodegradation, since these compounds are known to be persistent. Similar results were found by Olivella et al. (2006) with respect to PAH in riverine waters. These data are in agreement with values found at each sampling site taking into account time elapsed since the last fire (Figure 7).

The contribution of wildfires to the content of PAH in groundwater was demonstrated, as well as climatic conditions as a confounding factor on PAH levels detected. As water supplies may be vulnerable to disruption, increasing knowledge on water quality alterations due to forest fires is essential for development of decision criteria into management practices. This would enable scientists and stakeholders to work together to formulate effective management practices (Smith et al., 2011a, 2011b). These studies allow for a definition and presentation of a more accurate official list of organic pollutants, which is essential to propose new mechanisms for water treatment, in order to ensure quality and permit new environmental remediation strategies and human health promotion.

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