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Emerging contaminants related to the occurrence of forest fires in the Spanish Mediterranean



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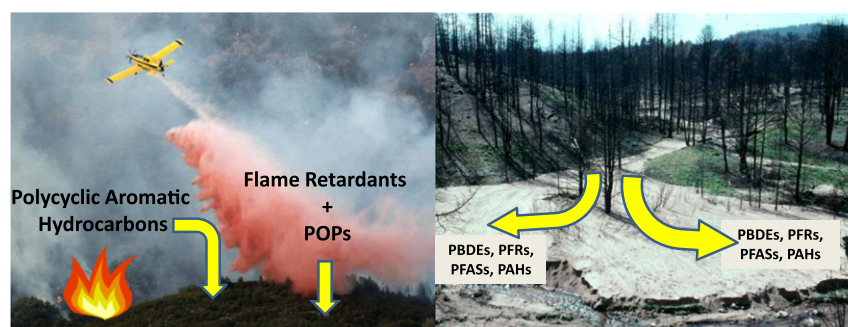
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HIGHLIGHTS

- Assessment of PBDEs, PAHs, PFRs and PFASs distribution in burned and unburned hillslopes
- BDE-85 concentrations were highest so no PBDE mixture was present in the fire extinguisher.
- The fire added significant PAH amounts into the soil (1256 ng g^{-1}), mainly in the upper 2 cm.
- PFRs and PFASs were found in both hillslopes with values up to 352 ng g^{-1} and 17 ng g^{-1} , respectively.
- Contaminants transport downslope in the erosion events depends on the compound nature.

GRAPHICAL ABSTRACT



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ABSTRACT

Forest fires can be a source of contamination because, among others, of the use of chemicals to their extinction (flame retardants, FRs), or by the production of Polycyclic Aromatic Hydrocarbons (PAHs) derived from high temperature alteration of organic matter. Up to our knowledge, this study is the first to assess the direct (PAHs 16 on the USA EPA's priority list), and indirect [tri- to hepta- brominated diphenyl ethers (PBDEs), organophosphorus flame retardants (PFRs) and perfluoroalkyl substances (PFASs)] contamination related to forest fires. The abundance and distribution of these contaminants were monitored on two Mediterranean hillslopes, one burned and one unburned, near Azuébar (SE Spain). Samples were taken in the foot, middle, and top of the slope, at two depths, and in two environments (under canopy and bare soil). Sediments were collected from sediment fences after erosive rainfall events. Most of the screened compounds were found in both, burned and control hillslopes, though significant differences were found between both. In burned soil, low concentrations of PBDEs (maximum $\Sigma 16 \text{ PBDEs}$: 7.3 ng g^{-1}), PFRs (664.4 ng g^{-1}) and PFASs (56.4 ng g^{-1}) were detected in relation to PAHs ($\Sigma 16 \text{ PAHs}$ = 1255.3 ng g^{-1}). No significant influence of the hillslope position was observed for any of the contaminants but differences based on depth and vegetation presence tended to be significant, particularly for the PAHs. After the first erosive event, concentrations of PBDEs and PAHs were higher in sediment than in soil (ΣPBDEs : 17.8 ng g^{-1} and $\Sigma 16 \text{ PAHs}$ = 3154.2 ng g^{-1}) pointing out the importance of connectivity processes, especially shortly after fire.

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1. Introduction

According to the International Panel on Climate Change, there is already a high degree of confidence that meteorological conditions associated to climate change will be propitious to increasing extreme events (IPCC, 2014). Impacts on land degradation will be manifested in bigger and more frequent wildfires, and greater water stress. Since 1982, the total area affected by forest fires in Mediterranean countries of the European Union (EU) has declined, and the number of fires tends to stabilize. However, in countries like Spain and Portugal, the trend has been slightly upward in the last 5 years (European Commission, 2015), and forest fires are becoming more frequent (Spano et al., 2014; Turco et al., 2016). Based on Spanish Environment Ministry reports (MAAM 2012, 2014), the mean number of fires in Spain during 2001–2010 was 17,127, burning an average of 113,848 ha of forest surface. In Valencian Community (located in the Mediterranean East of Spain), the average area burned in 1991–2010 was of 8706 ha yr⁻¹ but in 1994, 751 fires occurred, one of which burned >25,000 ha. In 2014, there were 92 wildfires in Valencia affecting 1800 ha of woody forest and 116 ha of forest herbaceous.

It is well known that environmental degradation processes are inter-related. One aspect of fire-induced ecosystem degradation that has drawn scientific interest recently is the chemical pollution related to forest fires. This contamination is associated either to the use of chemicals to their extinction known as flame retardants (FRs) (Pepper et al., 2011), or because pyrolysis or incomplete combustion of litter and standing vegetation favours the formation of toxic compounds as polycyclic aromatic hydrocarbons (PAHs) (Yuan et al., 2008). FRs are not only used to extinguish fires but also in the production process of electronics, furniture, clothes and cars (Boyles et al., 2017; Covaci et al., 2003, 2011). Perfluoroalkyl substances (PFASs) are widely used in aqueous film-forming foams (AFFF) but also in industrial and consumer products as protective coatings for textiles and paper, in the production of semiconductors and as polymer additives in herbicide and insecticide formulations and in cosmetics (Hale et al., 2017; Hu et al., 2016). AFFFs are usually spread over pool fires and they have limited post-fire security and are toxic groundwater contaminants (Hinnant et al., 2017). In general, AFFFs containing PFASs are not expected to be used in the extinction of forest fires. They are usually applied for suppression of combustion in industrial and commercial sites, and particularly in fire training areas (Hu et al., 2016). However, the possible presence and degradation of PFASs in relation to forest fires have been never measured. These compounds are persistent, bio-accumulative and/or toxic to wildlife and humans, as well as potential endocrine disruptors (Campo et al., 2016; Duan et al., 2015; Eulaers et al., 2014; Segev et al., 2009). Consequently, penta-BDEs, octa-BDEs, perfluorooctane sulfonate (PFOS) and perfluorooctyl sulfonyl fluoride (POSF) have been included as Persistent Organic Pollutants in the Stockholm Convention, and PAHs are candidates for their inclusion (UNEP, 2010). Additionally, in the EU to comply with the Water Framework Directive (WFD), Directive 2013/39/EU set the Environmental Quality Standards in the field of water policy for Priority Substances and other pollutants, including PAHs, which must be controlled to progressively reduce discharges and losses.

Brominated flame retardants (BFRs) account for a large group of FRs used for firefighting. Polybrominated diphenyl ethers (PBDEs) are the second highest production group of BFRs, and their presence has been reported in different environmental matrices as water (Wang et al., 2017; Ricklund et al., 2010); sediment (Ross et al., 2009); soil (Akortia et al., 2017) and biota (Eulaers et al., 2014; Boyles et al., 2017). In soils and sediments, photolytic degradation and debromination are possible (Segev et al., 2009; Lee and He, 2010). Debromination can be caused by microbial activity and can be harmful for the environment because lower brominated PBDEs are considered to be more toxic (Rodenburg et al., 2014). The sources of PBDEs contamination are leaching from a wide range of plastics, electronic equipment and textiles (Akortia et al., 2017; Covaci et al., 2011) or their incineration and subsequent

long-range transport in air. de Wit et al. (2006) reported their presence in living organisms and air of the Arctic. BDE-47, -99 and -209 are also present in sewage sludge (de Wit, 2002; Wu et al., 2017). The production and use of the most common PBDEs, penta- octa- and deca-BDE, is nowadays highly restricted in the USA and EU (Kemmlin et al., 2009). Despite PBDEs have been used for fire extinguishing (Alaee et al., 2003; Pepper et al., 2011) there are not published studies on their occurrence in relation to forest fires.

Since the ban on some BFRs, phosphorus flame retardants (PFRs) have been proposed as an alternative (van der Veen and de Boer, 2012). PFRs are widely used as plasticizers and anti-foaming agents in a variety of industries including plastics, furniture, textile, electronics, construction, vehicles and petroleum industries (Wei et al., 2015). Only few reports on possible PFR adverse effects have been published (Araki et al., 2014; Dishaw et al., 2011; Farhat et al., 2014; Kojima et al., 2013; Sun et al., 2016; Wang et al., 2015). Most of the recent research priorities have focused on the occurrence of PFRs in house dust, indoor and outdoor air, surface and ground waters, but data about their presence in soil and sediment after a forest fire are not available.

A small number of studies have already looked into PAH production in forest fires (Kim et al., 2003; Campo et al., 2011; Vergnoux et al., 2011; Choi, 2014). These studies have generally found a significant increase in soil PAH levels after fire, but, not so much to reach harmful levels. However, the increase could still affect local ecosystems (Pizarro-Tobías et al., 2015). In a fire, PAHs are formed by incomplete combustion of litter and standing vegetation (Kim et al., 2003), but they are also probably produced from soil organic matter (SOM). During fire only the upper few centimetres of soil could reach temperatures above 200 °C, at which formation of char and possibly PAHs starts (González-Pérez et al., 2004; Certini, 2005). Incorporation of partly burned organic material into the soil increases both its SOM (Campo et al., 2008) and PAH concentrations (Choi, 2014).

The produced PAHs are either volatilized or retained within the organic material from which they are formed. The volatilized PAHs may also become associated with organic material, as they easily adsorb onto litter, vegetation or floating ash particles (Kim et al., 2003; Choi, 2014). These organic materials are deposited on the surface forming a PAH-rich fire-litter layer (Johnsen and Karlson, 2007) and can become incorporated in the soil, increasing soil PAH levels. PAHs can also enter the soil by moving downwards in gaseous form, or by leaching from the fire-litter layer (Vergnoux et al., 2011; Choi, 2014). Several researchers have noted that most of the PAHs added with fire are removed from a location because the fire-litter, rich in both SOM and PAHs, is eroded downslope (Smith et al., 2011; Zheng et al., 2012; Luo et al., 2013). This eroded material would be transported to the streams as researched by Vila-Escalé et al. (2007), who stated that PAHs were more correlated with organic suspended substances than with total suspended substances.

The main of this study is to establish the impact of a high severity fire in a hillslope of Azuébar, Castellón (Spain) on the occurrence of PAHs and emerging POPs in soil and sediment from the burned area. Samples from coupled slopes (burned and unburned) were analysed and compared for PAHs, PBDEs, PFASs and PFRs concentrations. Furthermore, the specific objectives of the study are to (i) determine whether the fire occurred, in 2014, in Azuébar added significant amounts of PAHs and emerging POPs to the soil, (ii) establish possible relationships between concentrations and position on the hillslope, soil depth and presence of vegetation, and (iii) study the transport of the contaminants downslope. To our knowledge, this is the first report on the presence of flame retardants in burned soils.

2. Material and methods

2.1. Study site and sampling

This work was carried out in the municipality of Azuébar, Natural Park of Sierra de Espadán, in the Province of Castellón, Spain (Fig. 1).

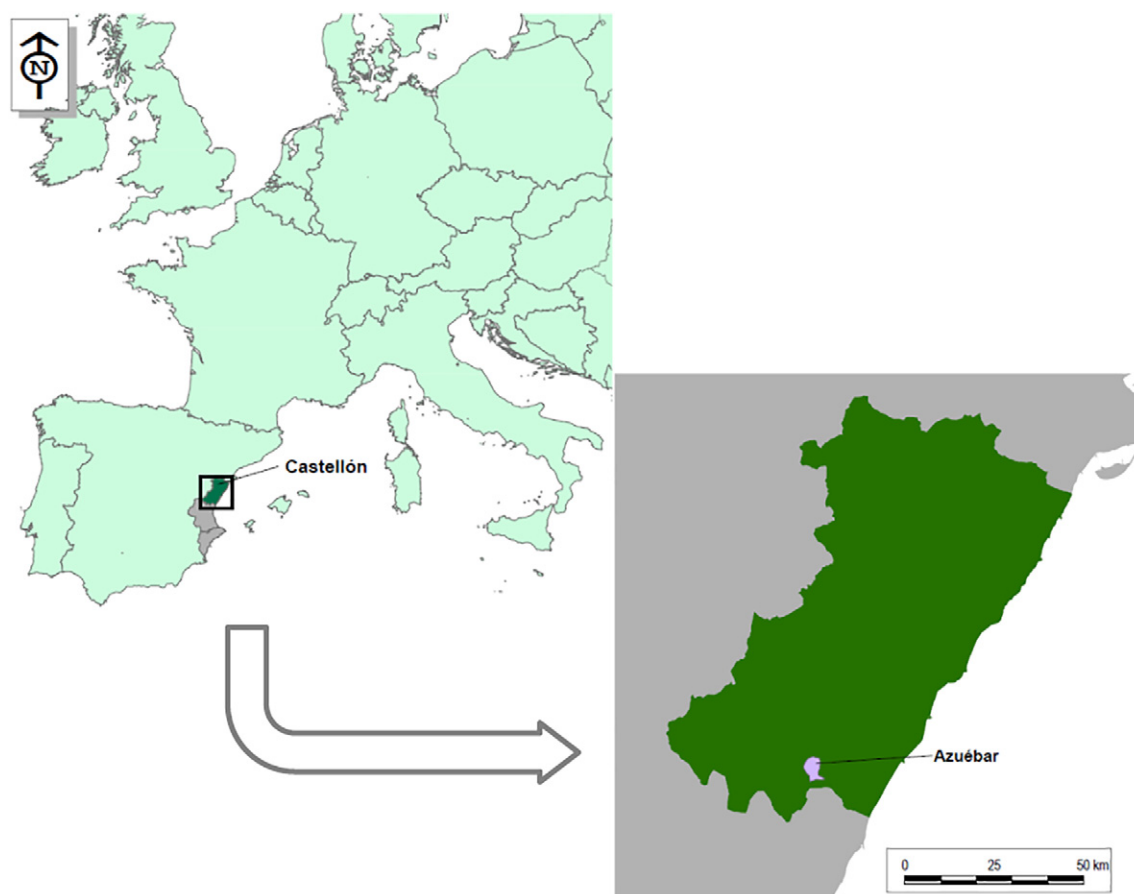


Fig. 1. Location of the study area. Coupled hillslopes in the municipality of Azuébar, Castellón (Spain), were used (Burned: 39°50'45.11"N, 0°22'20.52"W; Control: 39°51'08.7"N, 0°22'17.6"W).

Coupled hillslopes (burned: BU, and control: CO) belonging to the coastal foothills of the Iberian Mountain System were selected (BU: 39°50'45.11"N, 0°22'20.52"W; CO: 39°51'08.7"N, 0°22'17.6"W). Both slopes are located on forested concave hillsides, with ENE aspect, 25–28° of slope and an altitude around 370 m a.s.l. (more information is available in Supplementary information, SI, Fig. S1).

The climate of the area is meso-Mediterranean (mean annual precipitation of 450 mm), with a maximum precipitation in autumn (70 mm in October) and a second, but less rainy period in spring (45 mm in May). According to a close climatological station (Sot de Ferrer, 4.5 km from the hillslopes), the dry period (June–September), in which usually forest fires occur, presents a maximum temperature of 28 °C. The mean annual temperature is 16 °C (minimum of 5 °C approx.). Vegetation cover is characterized by a Mediterranean shrubland developed after recurrent wildfires in the zone. Soils are classified as Luvisol Chromic Skeletic type according to the FAO (2006), developed on Triassic dolomite, which show variable depth, always <50 cm thick, with 40% gravel content and clay-loam texture (Fig. S2).

Last wildfire on Azuébar municipality occurred on 28 August 2014 and burned 10.59 ha of forested area, according to the Emergency Coordination Centre of the Generalitat Valenciana. Eight air assets, as well as six emergency brigades participated in its extinction. About 70% of the affected area was in high- or moderate-high burn severity classes according to field burn indexes (Bento-Gonçalves et al., 2012). This municipality was affected by several wildfires during last years, registering up to five intentioned fires between 2012 and 2014.

Coupled Mediterranean hillslopes were sampled (19/09/2014) following a connectivity design according to which the top of the hillslope is the eroding zone, the middle part is the transport site and the foot's slope is the depositional zone (Bracken et al., 2015). Soil was taken in two environments (under canopy soil: UC; inter-plants or bare soil:

BS), and in two depths (TS: 0–2 cm and SS: 2–5 cm). Samples from each location, environment and depth (BU: $n = 12$; CO: $n = 12$; Table S1) were transported in sealed plastic containers, and dried at room temperature. All samples were dried at air temperature and sieved to <2 mm. Sediments were collected from four sediment fences constructed at the foot of the burned slope (Fig. S3). Sediment was negligible in the control hillslope, and samples could not be collected.

2.2. Sample extraction

The analysis for PBDEs was done simultaneously with the one for PAHs and the same with PFASs and PFRs analysis. Due to isomerism a total of 209 PBDE congeners is possible, but in this research only the abundance of some tetra-, penta-, hexa-, hepta-BDE congeners is assessed (Table S2). All soil and sediment samples were analysed for their concentrations of the 16 PAHs on the EPA's priority list, PFRs and PFASs listed in Table S2.

2.2.1. PBDEs and PAHs

Extraction of the PBDEs and PAHs from the samples was done by pressurized liquid extraction (PLE) using an ASE (Dionex ASE 200, Sunnyvale, CA, USA). Sample (2 g) were placed into stain steel extraction cell (6 cm) and sea sand (particle size 30–50 mesh, Fisher Chemicals) was loaded after the sample to avoid any void spaces. Both, PBDE and PAH internal standards (50 μL of each), were added before extraction. The PBDE internal standard contained three PBDEs (BDE-47, BDE-99 and BDE-153, which are tetra-, penta- and hexa-BDE congeners) ^{13}C labelled and dissolved in toluene. The PAH internal standard was a standard solution of the EPA's 16 PAHs, also labelled, in toluene (120 ng ml^{-1}). Two blank samples were prepared with only sand and internal standards to assess background noise and pollution during

the analysis process. The PLE was done using acetone/hexane (1:1) as solvent and with the following setting: pressure 1500 psi, temperature 100 °C, preheat time 5 min, heat time 5 min, static extraction time 10 min, flush 90%, purge time 120 s and 2 cycles.

The resulting extracts were concentrated to 0.5 ml by heating them in a sand bath and slowly evaporating with a Vigreux column. The extracts were cleaned up through a column packed with 1 cm of folded glass wool at the bottom, 6.75 cm hydrated Al₂O₃ (11% water) and 1 cm granulated Na₂SO₄, and eluted with 25 ml hexane. This method was successful in making most extracts clear and colourless. After the clean-up, the extracts were concentrated again with a Vigreux column to 1.0 ml. All extracts were stored dark, until analysis, to prevent degradation of the compounds. Finally, 100 µl of the extracts were pipetted into a vial suitable for GC–MS.

2.2.2. PFRs and PFASs

PFRs and PFASs were extracted by ultrasound solid-liquid extraction (US-SLE) using methanol as described in Lorenzo et al. (2015). Briefly, 5 g of sample was weighted into 50 ml polypropylene tubes. PFRs and PFASs isotopically labelled standards were spiked to the samples. Then, 10 ml of methanol were added to each tube and they were vortexed for 3 min, sonicated for 15 min and centrifuged for 5 min (950 rcf). The process was repeated three times. Finally, the sample was cleaned up by solid-phase extraction (SPE). This was performed by passing the samples through Phenomenex Strata™ C-18 cartridges and the compounds were eluted with methanol. The samples were evaporated to dryness under nitrogen stream, re-dissolved in 250 µl of methanol and transferred to a vial suitable for LC-MS/MS.

2.3. Determinations

2.3.1. PBDEs and PAHs

The determination was carried out with a Thermo-Quest Trace GC 2000 gas chromatograph (Thermo Fischer Milan, 176 Italy). Separation was performed using a fused silica column (J&W, 60 m × 0.32 mm i.d.) coated with DB-5 (film thickness 0.50 µm) and helium as carrier gas. Injection volume was 2 µl and injection temperature 60 °C (cold on-column injection), with a temperature programme reaching up to 320 °C. For details about the GC method see Table S3. The column was coupled to a Finnigan Trace mass spectrometer (MS) with the following operating conditions: 70 eV ionization potential of the electron impact source, 250 °C ion source temperature, and data acquisition in Selected Ion Mode (SIM). MS was set to start acquiring at 6 min.

Target compounds were identified using Xcalibur Software by interpretation of the mass spectra considering their retention times, and/or by comparison with literature data (Korytár et al. 2005). Quantitation of identified compound was done with internal standard methodology based on peak areas.

2.3.2. PFRs and PFASs

The analysis was carried out in a 1260 Infinity ultra-high-performance liquid chromatograph combined with a 6410 triple quadrupole mass spectrometer of Agilent Technologies (Santa Clara, CA, USA) with electrospray ionization (ESI). Compounds were separated with a Kinetex C₁₈ (50 × 2.1 mm, 1.7 µm) from Phenomenex (Torrance, CA, EEUU). For PFRs, ZORBAX Eclipse Plus C₁₈ was selected as trap column in order to control background contamination. The mobile phases consisted of (A) water and (B) methanol, both containing 2.5 mM ammonium fluoride for PFASs and 0.1% formic acid for PFRs. The flow rate was kept at 0.2 ml min⁻¹ throughout the run, and the sample volume injected was 5 µl. Analysis was performed in negative ion mode for PFASs and in positive ion mode for PFRs (instrumental characteristics are described in Table S4). Data acquisition was carried out in selected reaction monitoring (SRM) to identify and quantify using two precursor and product ion transitions (except for PFBA and PFPeA that gave only one transition), retention times, and the ratio of intensities between

the two product ions. Data were processed using MassHunter Workstation Software for qualitative and quantitative analysis (GL Sciences, Tokyo, Japan).

2.4. Quality assurance/quality control

The analytical methods were carefully validated. The LOD was calculated as the mass of analyte required to produce a signal-to-noise ratio (S/N) of 3:1, where the noise is calculated as the standard deviation of the background signal. The LOQ was also established as the concentration whose S/N was 10:1. Method LOQ values were in the range from 0.3 to 0.8 ng g⁻¹ dry weight (d.w.) for PBDEs, 0.2 to 2.8 ng g⁻¹ d.w. for PAHs, 0.3 to 2.5 ng g⁻¹ for PFRs and 0.83 to 3.33 ng g⁻¹ for PFASs.

Calibration curves were prepared daily obtaining R² > 0.98. Prior and after the batch (28 samples), calibration curves were constructed by injecting standards at different concentrations (2–20 ng ml⁻¹ for PBDEs and PAHs, 1–75 ng ml⁻¹ for PFASs and 1–300 ng ml⁻¹ for PFRs). Fig. S4 shows a chromatogram resulting from one of the external standard measurements. One instrumental and one procedural blanks as well as one spiked sample were analysed at the beginning and at the end of each batch to serve as quality control.

2.5. Statistical analyses

For the parametric analysis, normality of the data was tested using Shapiro-Wilk's test ($n < 50$) and homogeneity of variances was tested using Levene's test. Differences in the compound concentrations between treatments (BU, CO), hillslope positions (eroding, transport and deposition), environments (UC and BS) and depths (TS and SS) were established through analyses of variance with a General Linear Model (GLM), and confirmed *a posteriori* with the tests of Tukey's or *t*'student. Interaction of studied variables: treatment (T), position (P), environment (E) and depth (D) were also analysed. For non-parametric analysis, differences were determined by the tests of Mann-Whitney U (M-W) or Kruskal-Wallis (K-W). In all the cases, results were considered to be statistically significant at $p < 0.05$. The effect of soil organic carbon content on the contaminant distributions was quantified by calculating correlation relationships (Pearson's *r*) between these variables. All statistical analyses were carried out using IBM SPSS Statistics 22®.

3. Results

3.1. Soil

The hepta- and hexa-BDEs 153, 154 and 183 were not found in any of the soil samples. As shown in Table S5, concentrations of the detected tri- to penta-BDEs were in general low (the highest value was for BDE-85: 5.6 ng g⁻¹ d.w.). PBDEs were observed in both, BU and CO soils with sums of the PBDE values ranging from 0.5 ng g⁻¹ d.w. (CO) to 7.3 ng g⁻¹ d.w. (BU) (Fig. 2). The most frequent compound was BDE-47, which was found in all the burned samples and in most of the control ones. On the other hand, BDE-85 was only detected in the BU samples.

Concentration values of the individual compounds were not normally distributed, while their sum actually was it. According to the M-W test, only the BDE-85 values showed significant differences between BU and CO samples. None of the variables, slope position, vegetation and depth, have a significant influence on PBDEs levels individually, however decreasing trends were observed from transport, to erosion and finally to deposition zones. Similarly, in TS compared to SS, and in UC compared to BS. BU soils presented higher concentrations of the ΣPBDEs than CO ones ($p < 0.05$). Significant differences for the ΣPBDEs were not found based on the position, vegetation or depth. Interactions between these variables were not significant according to a GLM.

In general, all PAHs were found in BU and CO soils (Table S6). Only Acy and DahA are more frequent in BU soils. Concentrations ranged

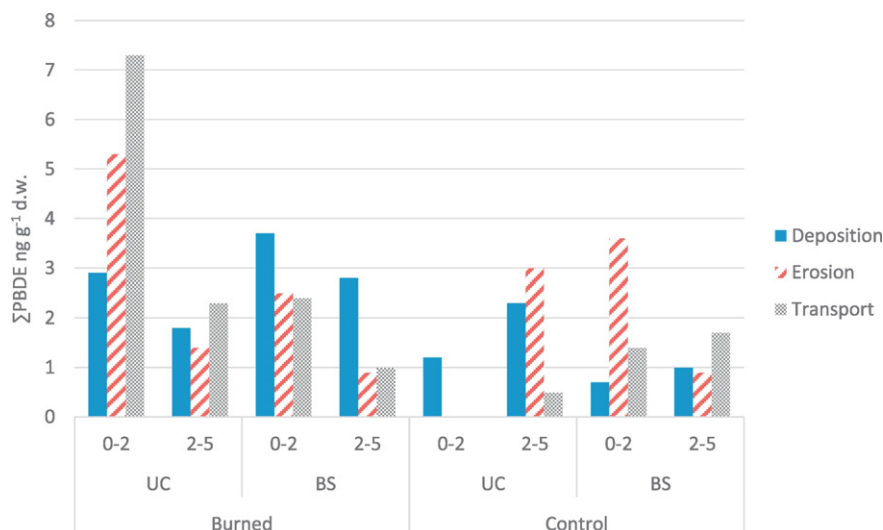


Fig. 2. Cumulated PBDE concentrations in the hillslope positions based on the different variables (Treatment: Burned, Control; Vegetation: UC: Under Canopy, BS: Bare Soil; Depth: TS: 0–2 cm, SS:2–5 cm).

from <LOQ (Acy) to 803 ng g⁻¹ d.w. (Nap). Despite the large variation of compounds as Nap and Phe, no clear outliers were found. Fig. 3 shows the total concentration of 16 PAHs in soil samples, reaching up to 1255.3 ng g⁻¹ d.w. in one of the burned hillslope TS samples. The proportion of light PAHs (2 and 3 aromatic rings) was higher in BU than in CO (Fig. 4a), indicating that these were the most produced by the fire. The heavy PAHs (4, 5 and 6 rings) were dominant in CO. The tendency in BU is actually dominated by just two light PAHs, Nap (2 rings) and Phe (3 rings).

Light PAHs and the Σ 16 PAH were not normally distributed whereas heavy PAHs followed a normal distribution. According to the M-W test, the BU slope had significantly higher light and Σ 16 PAH concentrations than the CO slope ($p < 0.05$). None of the other factors considered had a significant influence on their values. On the contrary, significant differences were obtained for the heavy PAHs in relation to treatment (BU > CO, $p < 0.05$) and depth (TS > SS, $p < 0.05$). For both, parametric and non-parametric tests, no significant differences associated to the slope position were found. Based on a GLM, double and triple interactions of the considered variables did not have a significant influence on the occurrence and concentration of PAHs in the area of study.

Regarding PFRs, TCEP, TPP, TDBPP and CDP were not detected in any soil sample. As shown in Table S7, TMPP was only found in one BU soil at low concentration (0.3 ng g⁻¹ d.w.). TDCIPP, TPhP and TEHP were at low concentration in both BU and CO soils (from 0.2 to 13.1 ng g⁻¹ d.w.). As for the rest of compounds, TCIPP, TnBP and TBEP were at high concentrations in BU and CO, being 319.8 ng g⁻¹ d.w. the highest value found for TnBP. Concentration values for PFRs were not normally distributed for any variable (depth, vegetation, slope position and treatment). Double and triple interactions of the studied variables did not have any significant influence on the occurrence of PFRs. However, Σ PFR concentration tended to be higher in CO than in BU soils (Fig. 5).

Some perfluorocarboxylates, short-chained (PFPeA, PFHxA and PFHpA) and long-chained (PFUnDA, PFTeDA and PFHxDA), and perfluorosulfonates (PFBS and ipPFNS) were not found in any sample. PFBA, PFDA and PFTrDA were only observed in BU soils (values ranging between 0.1 and 1.2 ng g⁻¹ d.w.). The higher value was detected for FOUEA (14.0 ng g⁻¹ d.w.). All PFAS concentrations can be found in Table S8. Σ PFAS was normally distributed and based on the t'student test, UC showed significantly higher concentration than BS ($p < 0.05$,

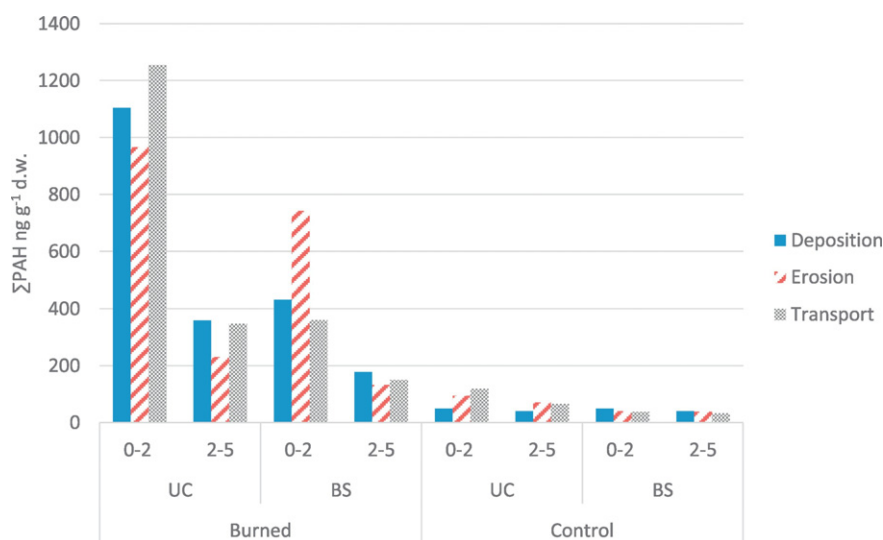


Fig. 3. Cumulated PAH concentrations in the hillslope positions based on the different variables (Treatment: Burned, Control; Vegetation: UC: Under Canopy, BS: Bare Soil; Depth: TS: 0–2 cm, SS:2–5 cm).

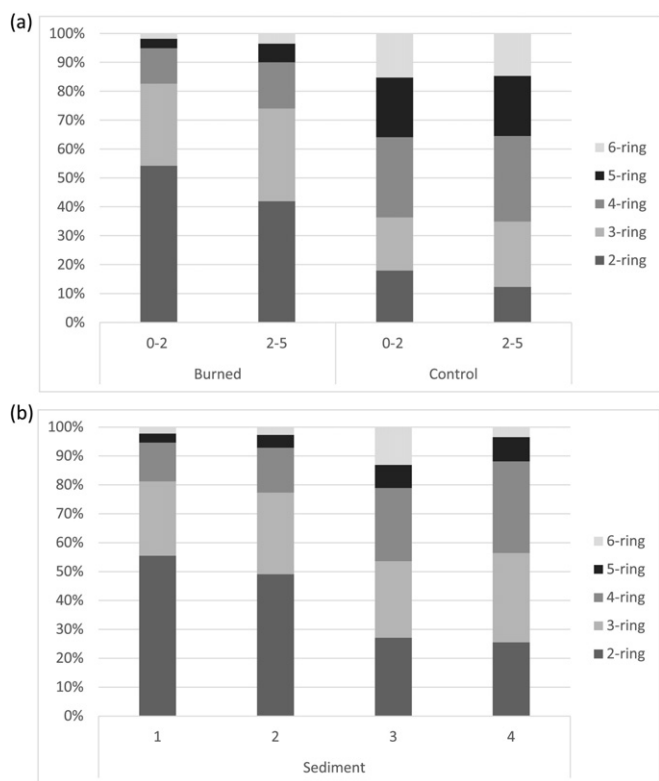


Fig. 4. Contribution of light (2–3 aromatic rings) and heavy (4–6 aromatic rings) PAHs in the: (a) burned and control soils (at different depths) and (b) sediment.

Fig. 6). The other variables considered (treatment, position or depth) did not present any significant influence individually as for double and triple interactions.

3.2. Sediment

Four erosive rain events were considered in this study. Based on the data of the closest pluviometer (Sot de Ferrer: 4.5 km), these were registered in 29/11/2014, 23/3/2015, 15–16/6/2015 and 2/11/2015, and produced 12.7, 143.6, 12.6 and 62.2 kg of sediment, respectively. These events did not produce any sediment in the CO hillslope.

As it was expected, BDE-153, – 154 and – 183 were not detected in the sediment samples (Table S5). Concentrations of the tri- to penta-BDEs were also low, but BDE-85 presented the highest value detected ($11.4 \text{ ng g}^{-1} \text{ d.w.}$). Only the BDE-47 was observed in all the sediment samples. The sum of the PBDE values was high in the sediment of the first erosive event ($17.8 \text{ ng g}^{-1} \text{ d.w.}$, Fig. S5), being higher than in soils ($7.3 \text{ ng g}^{-1} \text{ d.w.}$). These concentrations decreased up to one order of magnitude in sediments of the following events.

Similarly, the PAH concentrations in the sediments from the first event ($\sum 16 \text{ PAH} = 3154.2 \text{ ng g}^{-1} \text{ d.w.}$, Fig. S6) were higher than those found in soil ($\sum 16 \text{ PAH} = 1255.3 \text{ ng g}^{-1} \text{ d.w.}$). Concentrations also decreased in the sediments of the following events, but the main reduction (one order of magnitude) was observed in the samples of the third rainfall. The second rainfall event transported about ten times more sediment than the first and third events. The distribution of PAHs in the first sediment was very similar to that observed in the soil samples from the BU hillslope (Fig. 4b). Over time, however, the dominance of Nap and Phe decreased (Table S6).

As it was expected TCEP, TPP, TDBPP and CDP were not observed in the soil or sediment. On the other hand, TBEP, TMPP, TPhP found in soil samples were not present in sediment. TDCIPP and TEHP were only detected in sediment samples from the second event (23/03/2015) that was the most erosive one. TnBP showed the highest concentration ($26.5 \text{ ng g}^{-1} \text{ d.w.}$) and frequency. Conversely to other contaminants, the $\sum \text{PFR}$ in the first event was not higher than the values in soil samples (Fig. S7) but it decreased at the end of the studied period.

The perfluorocarboxylates, PFPeA, PFHxA, PFHpA, PFNA, PFUnDA, PFTeDA, PFHxDA and PFODA, and the perfluorosulfonates PFBS, ipPFNS and PFDS were not found in any soil or sediment sample. The PFBA, ipPFNA, PFNA, PFDoDA, PFODA, PFDS, PFHpS were present in soil but in sediment. The cumulated PFAS concentration was one order of magnitude higher in soil (maximum $\sum \text{PFAS} = 16.9 \text{ ng g}^{-1} \text{ d.w.}$) than in sediment ($\sum \text{PFAS} = 4.2 \text{ ng g}^{-1} \text{ d.w.}$, Fig. S8).

4. Discussion

According to the results, some of the detected PBDEs were abundant on both, BU and CO (Table S5). It was hypothesised that PBDEs would be preferentially found on the BU hillslope, because they were probably used for the forest fire extinction, in comparison to CO where there has not been a fire for at least 20 years. The occurrence of PBDEs on the CO might be related to atmospheric transport and deposition as stated by Eljarrat et al. (2008). These authors found concentrations of PBDEs

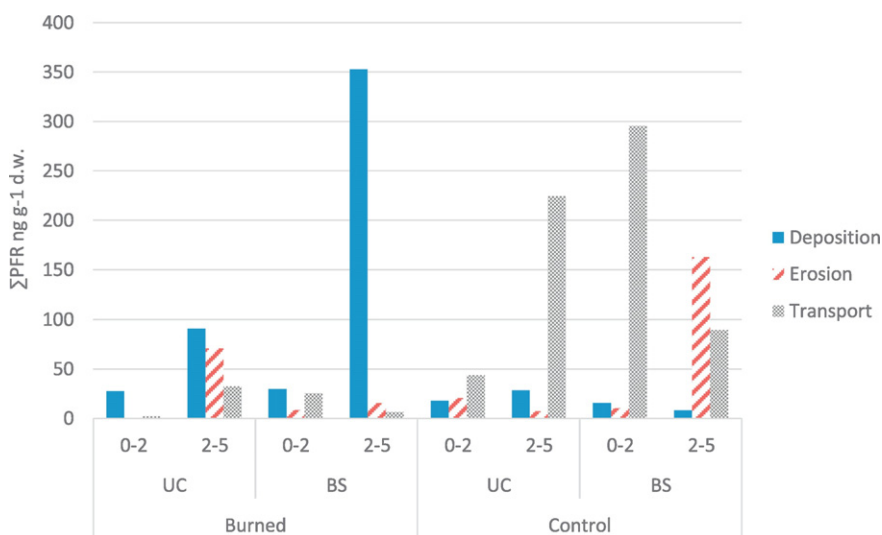


Fig. 5. Cumulated PFR concentrations in the hillslope positions based on the different variables (Treatment: Burned, Control; Vegetation: UC: Under Canopy, BS: Bare Soil; Depth: TS: 0–2 cm, SS:2–5 cm).

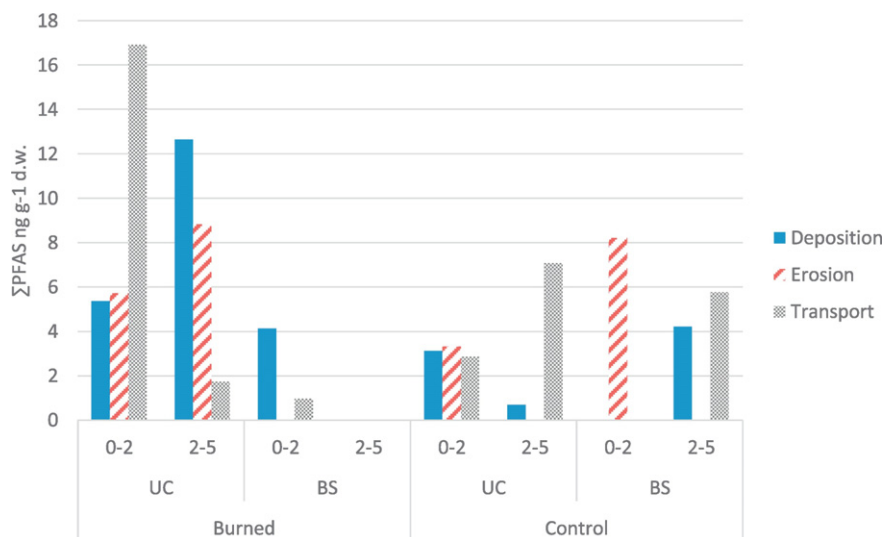


Fig. 6. Cumulated PFAS concentrations in the hillslope positions based on the different variables (Treatment: Burned, Control; Vegetation: UC: Under Canopy, BS: Bare Soil; Depth: TS: 0–2 cm, SS: 2–5 cm).

up to 0.84 ng g⁻¹ in reference soils used to study the effect of PBDEs-containing sewage sludge on agricultural soils, which was attributed to atmospheric deposition. In a similar research, Matscheko et al. (2002) used reference (non-treated) and sewage-sludge amended soils from three agricultural research stations in Sweden, and from two privately owned farms, and analysed them for BDE-47, -66, -99, -100, -153, -154 and -183. Concentrations in the reference soils from the agricultural research stations and two farm varied from 29 to 95 ng kg⁻¹ d.w. and 110 and 190 ng kg⁻¹ d.w. for Σ PBDE, respectively. Atmospheric deposition was also the main source of BDE-47, -99, -100, -153 and -154 in soil samples collected along a latitudinal transect through the UK and Norway, at remote/rural woodland and grassland sites, by Hassanin et al. (2004) who found concentrations in such samples ranging from 65 to 12,000 ng kg⁻¹ d.w.

Significantly higher concentrations of BDE-85 were detected in BU compared to CO (Table S5). Values of BDE-85, which is a penta-BDE, were also the highest of all PBDEs with a maximum of 5.6 ng g⁻¹ in soil, and 11.4 ng g⁻¹ in sediments. This might implicate that BDE-85 could have been used in the fire extinguisher. However, according to La Guardia et al. (2006) BDE-85 accounts for only 2–3% of the most widely produced penta-BDE mixtures. The largest contributors to these mixtures are BDE-47, -99, -100, -153 and -154 (La Guardia et al., 2006). These PBDEs were not found or were detected at low concentrations on the BU samples, probably degraded by high temperatures. There is a paucity of data in the literature related to BDE-85 occurrence in soils and sediment but, when measured, the levels found are often in the same range: 0.12–57 ng g⁻¹ d.w. in sewage sludge (Kupper et al., 2008; Davis et al., 2012; Lee et al., 2014; Venkatesan and Halden, 2014) and 0.016–0.151 ng g⁻¹ d.w. in sediment (Hlouskova et al., 2014). These previous BDE patterns should be taken into account with some caution because most of the available data on BDE congener patterns are from sediments and sewage sludge. Then, these patterns are little comparable to those obtained in soil before and after burning. Although Σ PBDEs was higher in BU than in CO, it is questionable whether a penta-BDE mixture was present in the fire extinguisher applied to the studied soil. As previously stated, the position on the slope did not have a significant influence on the distribution of PBDEs along the hillslope. However, in BU, two different trends were observed. In UC, PBDE values increased from erosion/deposition to transport sites, while in BS these tended to augment from erosion/transport to deposition depicting different connectivity tendencies in relation to the presence/absence of vegetation (Fig. 2).

Concentrations of BDE-85 tended to be higher at the TS than at the SS of BU (Fig. 2), in relation to the absence of rainfall in the period between fire occurrence and sample collection. This fact reduced the possibility of infiltration, and therefore of vertical distribution, and explain the very high concentration measured in the sediment sample of the first erosive event (Table S5). Vegetation did not significantly influence the distribution of PBDEs in the soil. However, the values of BDE-85 tended to be higher in UC than in BS. In Mediterranean areas, vegetation operates as an obstacle for erosion (acting as a sink) causing the accumulation of eroded soil (Urgeghe and Baptista, 2015). This eroded soil might transport contaminants, as proved the high concentrations found in this study, and can be the source of the PBDEs detected in under canopy sites. Beside this, a research conducted by Huang et al. (2011) proved that vegetation uptakes lower brominated PBDEs in a contaminated soil. When this vegetation is burned part of the contaminants that are not volatilized could be deposited on the soil and probably increased their concentration on these sites.

It is important to highlight the difficulty to ascertain the actual contamination of soils with PBDEs in relation to forest fires. PBDE concentrations in soils have been mainly investigated near electronic waste recycling sites and on agricultural fields where sewage sludge is applied as a fertilizer. For instance, at an electronic waste recycling site in Accra (Ghana) concentrations of Σ 13 PBDEs ranged from 15.6 to 96.8 ng g⁻¹ d.w. and BDE-28 was the dominant congener followed by -209 and -47 (Akortia et al., 2017). In Spain, BDE-209 has been widely used and high concentrations have been reported in sewage sludge and soils amended with sludge (*i.e.* Eljarrat et al., 2004, 2005, 2008; Gorga et al., 2013). Unfortunately, this congener was not analysed in this study and its levels cannot be compared with those reported elsewhere.

The fire in Azuébar indeed added significant amounts of PAHs to the soil (BU > CO, Table S6). The Σ16 PAHs reported here for BU are between 133.5 and 1255.3 ng g⁻¹ d.w. (Fig. 3), which are in agreement with the ones reported by Choi (2014). This author sampled pine bark, litter and soils from a burned site in Pohang, South Korea and obtained Σ 16 PAH concentrations of 5920 ng g⁻¹, 1540 ng g⁻¹, and 133 ng g⁻¹, respectively. In fact, PAH concentrations in BU are between those Choi obtained for soil and litter samples (considering the average of both soil depths since Choi's soil samples were taken at 0–5 cm). PAHs distribution in Azuébar's soil and Korea's litter are similar, suggesting that soils of this research could have incorporated significant quantities of burned organic material.

Similar results were also presented by Kim et al. (2003) who found a range of 150–1600 ng g⁻¹ in soils after several forest fires in the eastern coastal region of Korea. However, concentrations found in the present study are higher than the findings of Vergnoux et al. (2011) in repeatedly burned sites of the South of France (Σ 14 PAHs = 77–157 ng g⁻¹ d.w.) and the values reported by Pizarro-Tobías et al. (2015) after controlled fires in the Parque Natural de los Montes de Málaga (Spain) (400 ng g⁻¹ for Σ 15 PAHs). PAH patterns in burned soils are remarkably constant across studies and very similar to the one described here (Fig. 4a). In relation to Σ 16 PAH levels detected in CO (33.8–120.2 ng g⁻¹ d.w., Table S6), they are in the same order of magnitude than the values obtained by Pizarro-Tobías et al. (2015): average 58 ng g⁻¹, Kim et al. (2003): 49 ng g⁻¹, and Choi (2014): 26 ng g⁻¹.

According to the results, the position did not have a significant influence on the distribution of PAHs along the hillslope. However, a trend to accumulate PAHs in the middle of the hillslope was observed in both treatments (in BU the Σ 16 PAHs tended to increase from erosion to deposition and from this one to transport, while in CO from deposition to erosion and from erosion to transport). Despite significant differences were not found between TS and SS, for either the individual compounds or their sum, there must be some downwards movement during or shortly after fire, because PAH levels increased at both depths when BU and CO were compared (Fig. 3). No rain fell in the study area between fire and sampling, and therefore, gaseous movement could be responsible for this movement.

Despite partly burned vegetation is an important source of PAHs to the soil (Choi, 2014), there were not significant differences based on the presence/absence of vegetation. Loose PAHs that move downwards could be retained where vegetation was present (again sink effect). Soil in these vegetation patches had higher SOM levels already before fire, causing SOM and PAHs to increase together when the burned organic material is incorporated into the soil, though it is argued that the PAH production from SOM might be quite small (Kim et al., 2003).

The high PAH concentrations in the sediment of the first erosive rainfall suggest that erosion of burned organic material on the surface is an important process for PAHs transport since their profile in the sediments is similar to the one of burned soils. A sign of degradation and volatilisation may be responsible of the increasing dominance of heavy PAHs in the sediments over time. In the burned soil, the light, degradable PAHs probably declined in the months after fire as stated by Choi (2014). This would also lead to a lower contribution of light PAHs in the sediments (Fig. 4b). Accordingly, it is possible to state that the amount of PAHs moved downslope is thus not only dependent on the time since fire, but also on the intensity of the rainfall event.

Similar to PBDEs, it was hypothesised that PFRs would be mostly found on the BU hillslope, as consequence of their possible use as fire extinguisher, in comparison with CO hillslope. High potential for long-range atmospheric transport and persistence of PFRs would be responsible for their presence in the CO hillslope (Mihajlović et al., 2011; Wei et al., 2015).

For our knowledge, there are limited data about PFRs presence in sediment and soil and no data at all in these matrices related to forest fires. Other studies showed the presence of TCEP and TCIPP in sediments of two lakes from the Lazio Region in Italy (between <MQL and 0.5 ng g⁻¹ and between <MQL and 0.3 ng g⁻¹, respectively) and in sediments collected from the banks of the Tiber river and the Liri river, (TCIPP 0.4–32 ng g⁻¹ and TCEP <MQL–15 ng g⁻¹) (Cavaliere et al., 2016). TEHP and TPhP were also found at high concentration (2.1–290 ng g⁻¹) in sediment samples from the Spanish rivers Arga, Nalón and Besòs (Catalonia) and, as in this study, TCIPP was detected in most of the sediment samples with concentrations ranging from 13 to 365 ng g⁻¹ (Cristale et al., 2013). TBnP, TBEP, TCEP, TCIPP and TDCIPP were highly found as the main components in 28 sediment samples collected from three districts and the central part of Taihu Lake (China), with concentrations between 3.38 and 14.25 ng g⁻¹ (Cao et al., 2012).

These authors suggested as possible sources, the industrial wastewater discharge and domestic sewage.

Despite PFAS have been usually found in firefighting facilities, they have been never screened in an area affected by forest fires. Studies about PFAS concentrations in firefighting training facility sites showed high levels of PFOS, between 21 and 8520 ng g⁻¹ (Filipovic et al., 2015; Hale et al., 2017; Houtz et al., 2013; Kupryianchuk et al., 2016). These concentrations are far away from those found in this study which were between 0.1 and 1.7 ng g⁻¹ d.w., suggesting that PFASs were not present in the materials used to extinguish the forest fire. Presence and movement of volatile PFAS precursors in the atmosphere is frequently suggested as the principal distribution pathways of these compounds in the environment (Bossi et al., 2016; Lai et al., 2016; Strynar et al., 2012). Although discharges from wastewater facilities have also been commonly cited as PFAS sources (Campo et al., 2014; Hu et al., 2016) A global survey showed PFAS concentrations similar to those found in this research, with total PFCAs ranging from 0.03 to 14.3 ng g⁻¹ and PFASAs from <LOQ–3.3 ng g⁻¹ (Rankin et al., 2016).

There is scarce knowledge about sorption of PFASs in soil and their distribution in the mineral and organic phases. Some factors as the type of mineral and the charge are crucial for PFAS sorption in the environment, affecting their leaching, transport and bioavailability (Hellsing et al., 2016). These authors showed that the sorbed PFASs could easily be desorbed by gentle rinsing with water, and so by rainfall the more water-soluble PFASs can be released and leach into groundwater or be taken up by plants, explaining to a certain point the lower concentrations found in sediment with regard to soil in this study and the higher concentrations of PFAS in UC than in BS.

Despite the increased PAH values in the burned hillslope, concentrations were not harmful. In Spain, there is no legislation regulating the admissible levels of these contaminants in soil. In the Netherlands, for instance, standards for soil quality give a maximum value of 1500 ng g⁻¹ for 10 specific PAHs (Nap, Ant, Phe, Flu, BaA, Chr, BaP, BghiP, BkF and Ind) if soil is to be used in a residential area, but pollution is considered dangerous at 40000 ng g⁻¹ (RIVM, n.d.) The highest levels measured in this study for these 10 PAHs were found in a burned soil sample located in the transport zone (UC, TS) and in the first sediment sample, with 1100 and 2800 ng g⁻¹. These are far below the dangerous limit. For individual PAHs, Kalf et al. (1995) estimated maximum permissible concentrations (MPC) for soil, which should protect 95% of the species in an ecosystem. Only the MPC value for naphthalene proposed by Kalf et al., 1995 (140 ng g⁻¹) was exceeded in Azuébar; however, levels at which species are acutely affected are probably much higher than this MPC. It can be stated that at some parts of the slope, PAH levels could be possibly harmful to humans and animals if they are exposed for long periods of time.

Some processes, however, might increase pollution hazard after fire. Firstly, the results show that erosion processes can concentrate PBDEs and PAHs locally where sediments are deposited. Secondly, PAHs could accumulate in the soil with recurrent fires. Light PAHs can be produced by fire in such amounts that their levels remain elevated for years despite their degradability (Vergnoux et al., 2011). Heavy PAHs, even though produced in small amounts, can also remain in the soil for long periods of time (Duan et al., 2015). The persistence of heavy PAHs could explain their relatively high levels in the control soils, which may be a remnant of a fire occurred in the past. Although fire frequency was not found to be a very good predictor of PAH levels (Vergnoux et al., 2011), the possibility of PAHs accumulating with frequent fires cannot yet be ruled out.

Table S9 shows the relationships between soil organic carbon (SOC) and the sum of the concentrations of the different families of contaminants in soil samples. Altogether and in CO, only PAHs presented a significant correlation with SOC. In BU, both PAHs and PBDEs were significantly correlated to SOC content. These correlations between SOC and PAH levels supports the influence of vegetation patches in the distribution of these compounds. At both slopes, more SOC is

associated with more PAHs. This is in line with the image of high-PAH organic material being added to the soil during fire.

It should be noted that the sampling group used in this research was relatively low. Additional research on soil composition and microbial behaviour is required to assess the effects of the contaminants. A next step for research should be to find out if the contamination in soil and sediment actually affects the capability of ecosystems to regenerate from fire. The low number of samples limits the conclusions that can be drawn about the compounds distribution at the hillslope scale, the depth effect and the vegetation influence. Additional research with more sampling points and more replicates per treatment would help to create a deeper understanding of the mechanisms involved in POPs contamination related to fires impact.

5. Conclusions

The fire in Azuébar actually added significant amounts of PAHs to the burned soil. Mainly, the upper soil layer was affected, and vegetation patches generally tended to have higher concentrations. Besides depth and canopy presence, soil organic carbon was important in the occurrence and distribution of PAHs. PBDE values were relatively low on the burned slope and most of the concentrations found can probably be related to atmospheric deposition, because these contaminants were also found on the control hillslope. PBDEs seemed to be more abundant in the top layer of the soil. It is questionable whether a PBDE mixture was applied to the burned hillslope due to the fact that BDE-85 values were highest, and the penta-BDE mixture contains twenty times more BDE-99, which showed low concentrations here, than other compounds. PFRs and PFASs concentrations in this study were similar to those found in others not related to fires, suggesting that these compounds were not used in this forest fire. In the case of PFASs, significant differences have been found between under canopy and bare soils. Further studies about the presence of vegetation and bioremediation should be done.

There was no clear pattern for the distribution of screened contaminants over the different slope positions, though higher concentrations tended to be found on the transport and deposition levels. In comparison to the soil, the sediments transported downslope contained significant amounts of PBDEs and PAHs pointing out the importance of connectivity processes. The contaminants enrichment in the first post-fire sediments was related to movement of burned organic material.

Concentrations of the different compounds seem to be low, and therefore the contamination from a fire like the studied here is unlikely to directly harm ecosystems. However, PAHs might accumulate in the soil with recurrent fires, and substantial inputs to other ecosystem compartments may happen with the first rains after fire. Erosion processes can concentrate contaminants on the lower parts of the hillslope, or in the valley, leading to bioaccumulation and potentially hazardous values in higher trophic levels.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2017.06.005>.

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