Impact of Forest Combustion on Soil Contamination by PAHs Using QuEChERS and GC-MS/MSTQD

Abstract

The present study was conducted in one of the most densel~~y~~ forest area of Asir region located in the southwest of Saudi Arabia to study the Impact of Forest Combustion on surface and subsurface Soil Contamination by Poly Aromatic Hydrocarbons (PAHs). The extraction and analytical methods, has been developed and validated for quantification of trace levels of 17 PAHs namely, Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Retene, Benzo[b+j]fluoranthene, Benzo(a)pyrene, Benzo[k]fluoranthene, 3-methylchol-anthrene, Dibenz[a,h]acridine, Indeno[1,2,3-cd]pyrene, Dibenz[a,h]anthracene and Benzo[ghi]perylene. Surface and subsurface soil samples collected from Alsaqa and Murir post~~-~~fire forests in Asir Province, Saudi Arabia, and extracted by Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) and analyzed by Gas Chromatography-Mass Spectrometry Triple Quadrupole (GC-MS/MSTQD). The experimental results of 17 compounds of PAHs were highly satisfactory linearity, recovery and precision, especially with the tested soil samples. Recovery % ranged from 96.48±2.19 to 105.61±3.21 %., the limit of detection (LOD) ranged from 3.71 to 6.77 µg kg^{-1}. M~~, m~~eanwhile the limit of quantification (LOQ) for the analyzed PAHs were in the range of 10.47 to 16.42 µg kg^{-1}. This method featured good sensitivity, quantification limits were low enough, and the precision of the analyzed 17 PAHs. The calibration curves were linear over wide concentration ranges with correlation coefficients (r2) 0.7478 to 0.9822 for 17 PAHs analyzed by GCMSMSTQD. The concentrations of the investigated PAHs in Alsaqa forest surface (S) and subsurface (SS) soils ranged from24.81±4.29 to 57.28±3.56 and 24.10±2.31to 55.47±4.15 mg kg^{-1}dry weight respectively. Meanwhile, the PAHs concertation in Murir surface and subsurface soils ranged from 12.48±2.37 to 28.83±3.35 and 12.83±1.37 to 25.59±4.31 mg kg^{-1}dry weight respectively. Retene compound was~~ere~~ detected in Alsaqa, and Murir forest investigated surface, and subsurface soil sample ranged from 57.28, 55.47, and 28.83, 25.59 mg/kg^{-1}(ppm) respectively. Meanwhile, Retene was not detected (ND) in the control surface and subsurface soil sample. The detected PAHs by applying the modified QuEChERS and GCMSMSTQD method were applied successfully for the extraction and determination of the 17 PAHs in burned forest soil samples.

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Keywords: Polycyclic aromatic hydrocarbons PAHs, Soil, Forest, Combustion, QuEChERS and Contamination

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic contaminants, which exist ubiquitously in the environment and comes from natural processes such as forest fires, volcanic activity contributing to the background values of PAHs and anthropogenic activities.The effects of forest fire on the level and distribution of PCDD/Fs and PAHs in the soil, the levels of PCDDyFs and PAHs in the soil are raised due to deposition of ash covered with adsorbed PCDDy Fs and PAHs **[1]**. The Effects of fire on properties of forest soils cause significant removal of organic matter, deterioration of both structure and porosity, considerable loss of nutrients through volatilization, ash entrapment in smoke columns, leaching and erosion, and marked alteration of both quantity and specific composition of microbial and soil-dwelling invertebrate communities. **[2]**. Evolution of the Concentrations of PAHs levels fell along the months in burnt woodland soils. The total PAHs level from 188 to 119 μg/kg), apparently as the result of rainfall and the prevention of further input from the atmosphere by the overlying layer of wood ash, which had a very high PAH adsorption capacity (1169 μg/kg) and did not itself appear to act as a source of PAHs. PAH transport may have been assisted by increased mobilization of PAHs associated with dissolvable organic matter due to an increase in soil pH due to alkaline ash components **[3].**

Levels and patterns of PAHs in pine bark, litter, and soil after a forest fire are normalized by organic carbon (OC) fractions, also showed decreasing trends, indicating a direct influence of the forest fire. Among the 16 targets PAHs, naphthalene was a dominant compound for all types of samples. Light PAHs with 2–4 rings significantly contributed to the total concentration, and their contribution decreased in the course of time**[4].** Levels and patterns of PAHs in soils after forest fires in South Korea clearly suggests that soils in the forest-fire region can be contaminated by PAHs directly emitted from biomass burning. However, the fire-affected soils can return to the pre-fire conditions over time through the washout and wind dissipation of the ash with a high content of PAHs as well as vaporization or degradation of light PAHs **[5].**
Sources, Behavior, and Indication of PAHs in soils significance of only 16 compounds regulated by the US EPA, the geochemical fate of numerous PAH derivatives in soils. The indication potential of PAHs has still not been completely revealed by now, as well as the relationship of these compounds with the humus and hydrocarbon statuses of soils **[6]**. The values of PAH isomeric diagnostic ratios indicated that forest soil PAHs were mainly originated from traffic emissions, mixed sources and coal/wood combustion in the urban, suburban and rural areas **[7].**

PAHs in Soil Organic Horizons Depending on the soil burn severity and type of ecosystem. An association between the low molecular weight PAHs and 50% burn-off temperature differential scanning calorimetry supports the idea of fire smoke as the main source of low molecular weight PAHs in charred biomass generated at temperatures of 200–400 °C**[8]**. The fate of polycyclic aromatic hydrocarbons at a forest fire site using a conceptual model based on field monitoring. Light PAHs were dominantly emitted from the forest fire, but they showed higher decreasing rates with total precipitation **[9].**

Surface soils affected by forest fires from Igbanko mangrove forest in Nigeria were analyzed for 16 EPA priority polycyclic aromatic hydrocarbons (PAHs) using gas chromatography–mass spectrometry (GC–MS). The total PAHs concentrations in the soils ranged from 63 to 188 mg/kg 1 dry weight. The three predominant PAHs in the soils were naphthalene (Na), fluoranthene (Flu), and benzo(b)fluoranthene (BbF). Compared to the control sample (19 mgkg 1), elevated PAHs concentrations were observed in the soils, an indication of some level of PAHs contamination **[10].**

A Quick, Easy, Cheap, Effective, Rugged andSafe (QuEChERS) method has been adapted and validated for the simultaneous analysis of 16 PAHs, in sediment. The obtained concentrations are in good agreement with the certified values with recoveries ranging 60 %–103 % for most of PAHs. [**11, 12,13].** Retene (1-methyl-7-isopropylphenanthrene) is often used as a marker for softwood combustion and for polycyclic aromatic hydrocarbon (PAH) source apportionment. **[14].**

In this study, modified QuEChERS techniques used for the extraction and clean-up procedure followed by GCMSTQD for the analysis of PAHs in 2 burned forest and control soil samples to evaluate the impact of PAHs concentration in burned and unburned soil form Asirforests located in the southwest of Saudi Arabia.

Material and Methods

Standards and Reagents

Calibration and injection standards of PAHs with declared 99.9% purity, were purchased from AccuStandard, 153 Inc., New Haven, CT, the USA as an individual (50 mg) or mixture standards at a concentration of 100µg/mL. Internal standards are ^{13}C 12-labelled;~~,~~ the use of the ^{13}C-labelled compound is preferable because the analysis can be quantified without clean-up. All solvents (Methanol, dichloromethane, hexane and acetonitrile) used for the extraction and analysis PAHs were residue-analysis grade 99.9 % purity and obtained from Fisher Scientific (Fair Lawn, NJ, USA). QuEChERS kits were~~as~~ purchased from Phenomenex, Madrid Avenue, Torrance, CA, USA.

Study Area and Samples Collection

Soil samples were collected from tow combustion forest in Asir region, (Capital of Abha, the total area of 76,693 km^2, a total of the Population in 2018 was2,478,347), located in the southwest of Saudi Arabia Fig (1). Twenty soil samples (10 surfaces from1-10 cm and 10 subsurface samples from 11-20cm) were collected from Alsaqa forest in Abha, and Murir forest in An-Namas was burned in 2018, and 2017 respectively. The distance between both forests was 147km. Plank soil samples (Control) were taken from Billahmar unburned forest, which is far from the mentioned forests 70kmin same region. Juniperus(*JuniperusProcera* and *JuniperusProcera*) were the dominant plant in the investigated forests.

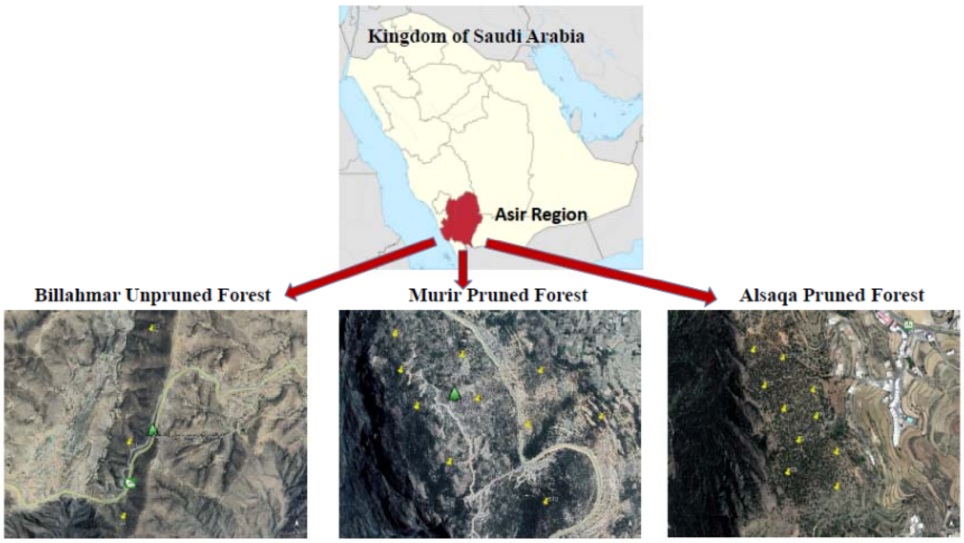

Figure (1) Soil samples collected from Alsaqa, Murir burned forest and Billahmar unburned forest (Control) in Asir region, located in the southwest of Saudi Arabia.

Physicochemical properties analysis.

Electrical conductivity (EC), pH, and soluble cations and anions were analyzed in saturated soil paste **[15].** Particle size distribution was determined according to the method reported by **[16]** using a hydrometer. Calcium carbonate was determined by following the procedure of **[17].** While organic matter contents were assessed using the Walkley-Black method **[18].**

Samples Preparation and Extraction by QuEChERS

Soil samples were dried and saved by 10 ml mish sieve. To extract the PAHs, 10 gm soil sample (≥83% H_2O content) into a 50 mL centrifuge tube. Alternatively, weigh 3 g air-dried soil sample into a 50 mL tube, then adding 7 mL H_2O, vortex briefly, and allow to hydrate for 30 minutes, add 10 mL of acetonitrile to each sample. Shake (manually or mechanically) or vortex samples for 5 minutes to extract the PAHs. (SpexSamplePrep Geno/Grinder 2010 operated at 1500 rpm was used). The contents of ECQUEU750CT-MP (citrate salts) Mylar pouch were added to each soil samples in the centrifuge tube. Immediately shake samples for at least 2 minutes and centrifuge for 5 minutes at ≥ 3500 rcf.

Sample Cleanup

Transfer a 1.5 mL aliquot of supernatant to a 2 mL CUMPSC18CT ($MgSO_4$, PSA, C18) dSPE tube. Vortex samples for 2 min, and centrifuge for 2 min at high rcf (e.g. ≥ 5000). Filter purified supernatant through a 0.2 µm syringe filter directly into a 1.8ml umber GC vial. Finally, PAHs in the extracted soil samples were analyzed by GC-MS/MSTQD.

Analysis by GCMSMSTSQ 8000/SRM

All measurements have been carried out using the latest Thermo Scientific™ TSQ 8000™ triple quadrupole GC-MS/MS system equipped with the Thermo Scientific™ TRACE™ 1310 GC with SSL Instant Connect™ SSL module and Thermo Scientific™ TriPlus™ RSH auto sampler. Injection mode was spiltless, Splitless Time 1.0 min GC Column DB5 MS, 30 m × 0.25 mm × 0.25 µm.Carrier gas was He99.999 %, flow rate 1.2 mL/min, constant flow, temperature program 100 °C, 1 min; 10 °C/min to 160 °C, 4 min and 10 °C/min to 250 °C, 2 min, transfer line temperature 280 °C, total analysis time 31 min, TriPlus RSH Autosampler Injection volume 1 µL. Ionization mode EI, 70 eV, Ion source temperature 250 °C, scan mode SRM using timed SRM SRM transition setup automatically build-up by AutoSRM software. GCMSMSTQD 8000 SRMTransition conditions are shown in (Table 1).

Table 1: GCMSMSTQD 8000 SRM Instrumental conditions of PAHs analysis in soil samples.

GC Trace Ultra Conditions		TSQ Quantum MS/MS Conditions	
Column	DB5 30 m × 0.25 mm × 0.25 µm	Operating mode	Selected Reaction Monitoring (SRM)
Injector	Splitless	Ionization mode	EI
Injected volume	1 µL	Electron energy	70 eV
Injector temperature	220 °C	Emission current	50 µA
Carrier gas	Helium, 1.2mL/min	Q1/Q3 resolution	0.7 u (FWHM)
Oven program	70 °C hold 1 min 15 °C/min to 150 °C hold 1 min 2.2 °C/min to 220 °C hold 1 min 5 °C/min to 285 °C hold 5 min Run Time 30.00 min	Collision gas	Argon
Transfer line temperature	280 °C	Collision gas pressure	1 mTorr
		Polarity	Positive

Method Performance

Precision and accuracy of the extraction and analysis method were conducted by3 replicates of blank soil sample spiked with the labelled PAHs standards. Limit of detection: Instrument

Detection Limit (IDL), Sample Detection Limit (SDL), Method Detection Limit, accuracy and precision

QAQC Strategies

Quality control samples were~~as~~ prepared and analyzed the duplicate sample, blank and spiked, and/ or Certified Reference material CRM was prepared for this purpose and processed with every~~ach~~ 5 samples. QuEChERS and GCMSMS TSQ 8000 method limit of detection (LOD) and Limit of Quantification (LOQ), repeatability, reproducibility, accuracy and precession also were determined for each PAHs compound.

Results and Discussion

Seventeen PAHs (Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Retene, Benzo[b+j]fluoranthene, Benzo(a)pyrene, Benzo[k]fluoranthene, 3-methylchol-anthrene, Dibenz[a,h]acridine, Indeno[1,2,3-cd]pyrene, Dibenz[a,h]anthracene and Benzo[ghi]perylene) were tested in Surface and subsurface soil samples collected from Alsaqa and Murir post-fire forests in Asir Province, Saudi Arabia, and extracted by Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) and analyzed by Gas Chromatography-~~—~~Mass Spectrometry Triple Quadrupole (GC-MS/MSTQD). Also, physicochemical properties of investigated surface and subsurface burned and control soil samples were tested.

Physicochemical properties of burned forest soils samples.

In general, soils in forest Alsaga and Murir have higher values of chemical soil properties (EC, CEC, OM and CaCO3) compared with unburned soil. The soils in forest Alsaga and Murir have higher OM content ranged from (9.20% to 12.4%) compared with control soil (1.12% to 5.24%). Also, the soils in forest Alsaga and Murir have medium values of EC varied from 1.46 dS m-1 to 2.16 dS m-1 while control soil low in EC (0.78 dS m-1 to 0.87 dS m-1. The results indicated that~~,~~ the soils in forest Alsaga and Murir have higher CEC values ranged from (31.4 -35.5 cmol/kg) compared with (17.1-18.5 cmol/kg) in control soil. The soils in forest Alsaga and Murir was silt loam in texture while sandy loam or loam in control soil. Fire leads to changes in the chemical properties of soil, particularly the quantity and quality of OM, availability of nutrients, CEC, and base saturation **[15].** The findings of our study were similar to those previously reported in the literature **[16, 17]** although with some variation as showed in table (2) and Fig. (2).

Table 2. Selected physicochemical properties of burned forest soils in Asir region.

Forest	pH		CEC cmol/kg		OM %		EC (dS m^{-1})		$CaCO_3$ %		Clay %		Sand %		Sand %	
	S	SS	S	SS	S	SS	S	SS	S	SS	S	SS	S	SS	S	SS
Alsaqa	7.3	7.2	31.8	35.4	10.2	9.1	2.0	2.1	7.4	2.0	16.9	16.7	29.5	40.5	53.6	42.8
Murir	7.1	7.0	31.7	31.4	12.1	12.3	1.4	1.4	0.2	0.3	15.7	18.0	31.9	29.5	52.4	52.4
Control	7.2	7.1	17.1	18.5	1.1	5.2	0.7	0.8	0.3	0.3	14.5	18.9	57.5	39.5	28.0	41.6

(S= Surface soil SS= Subsurface soil)

QuEChERS and GC MS/MSTQD for analysis of 17 PAHs.

Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) as a simple and rapid extraction method and GCMSMSTQD as a determination techniques of 17 PAHs compounds in forest burned soil samples. Retention time, LOD, LOQ, recovery % and a target mass of SRM scanning mode was determined as showmen in the table (1). The results clearly reflect the developed and modified QuEChERS method offers an extraction efficient and easy sample preparation procedure for the determination 17 PAHs in soil samples investigated in this research. Recovery % ranged from 96.48±2.19 to 105.61±3.21%., the limit of detection (LOD) ranged from 3.71 to 6.77 µg kg^{-1}. M~~, m~~eanwhile the limit of quantification (LOQ) for the analyzed pesticides were in the range of 10.47 to 16.42 µg kg^{-1}. A Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) method has been adapted and validated for the simultaneous analysis of 16 PAHs, in sediment. The obtained concentrations are in good agreement with the certified values with recoveries ranging 60 %–103 % for most of PAHs. [**11, 12, 13]** The proposed method featured good sensitivity, quantification limits were low enough, and the precision of the analyzed 17 PAHs. The calibration curves were linear over wide concentration ranges with correlation coefficients (r2) 0.7478 to 0.9822 for 17 PAHs analyzed by GCMSMSTQD. In addition, the SRM chromatograms demonstrated high selectivity with no significant interferences observed and an excellent signal/noise ratio (> 5:1) for all tested PAHs as showmen in (Figure 1).

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Table (3) Retentions times (Rt), monitored target, LOD, LQD, qualified ions and Recovery% for SRM mode GC-MSMSTQD of 17 PAHs.

No	**Compound**	**Rt**	**Target ion**	**Q1**	**Q2**	LOD	LOQ	r^2	**Recovery%±SD**
1	Naphthalene	9.46	128	129	127	4.52	10.47	0.9452	103.28±2.78
2	Acenaphthylene	13.89	152	153	151	4.66	12.71	0.9216	96.48±2.19
3	Acenaphthene	15.43	154	153	152	5.08	13.22	0.9584	101.28±2.71

4	Fluorene	16.28	166	165	163	6.26	14.56	0.8335	99.84±2.33
5	Phenanthrene	17.89	178	176	179	6.51	15.38	0.9603	105.61±3.21
6	Anthracene	23.41	178	176	179	6.77	15.48	0.8126	99.445±2.81
7	Fluoranthene	24.34	202	200	203	5.88	14.29	0.9362	98.77±3.21
8	Pyrene	24.69	202	200	203	4.21	12.67	0.9822	102.58±2.72
9	Retene	25.63	220	219	233	5.37	13.89	0.9168	98.87±2.56
10	Benzo[b+j]fluoranthene	27.78	252	253	250	6.52	16.38	0.9713	99.81±4.55
11	Benzo(a)pyrene	30.12	252	253	250	4.22	12.47	0.9180	98.39±2.05
12	Benzo[k]fluoranthene	34.19	252	253	250	3.71	13.49	0.9452	97.38±3.28
13	3-methylcholanthrene	34.22	268	269	266	4.38	14.41	0.8452	96.88±3.43
14	Dibenz[a,h]acridine	35.09	279	280	278	4.91	15.59	0.8556	101.91±3.77
15	Indeno[1,2,3-cd]pyrene	35.49	276	277	274	6.49	17.23	0.8231	99.48±3.09
16	Dibenz[a,h]anthracene	35.81	278	276	279	5.99	16.42	0.7478	104.61±3.22
17	Benzo[ghi]perylene	35.94	276	277	274	4.67	15.87	0.8556	98.87±3.44

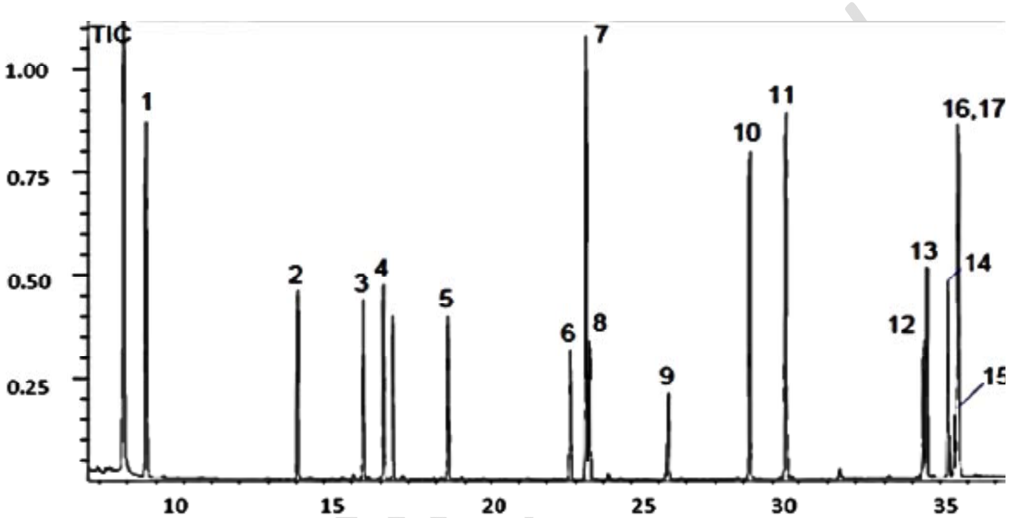

Fig. (3) Retentions times (Rt) for SRM mode GC-MSMSTQD of 17 PAHs.

PAHs concentration in forest burned and control soil.

The concentrations of the investigated PAHs in Alsaqa forest surface (S) and subsurface (SS) soils ranged from 24.81±4.29 to 57.28±3.56 and 24.10±2.31to 55.47±4.15 mg kg^{-1}dry weight respectively. Meanwhile the PAHs concertation in Murir surface and subsurface soils ranged from 12.48±2.37 to 28.83±3.35 and 12.83±1.37 to 25.59±4.31 mg kg^{-1}dry weight respectively. On the other hand, there is no detected PAHs except Naphthalene and Fluorene in unburned control soil sample as shown in Table 4 and Fig. 4, 5 and 6. The mean concentrations of

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individual PAHs in Alsaqa forest burned surface and subsurface soil sample are shown in Table 1 and Fig 4. The PAHs distributions in all the samples were dominated by Retene, Naphthalene, Fluorene, Acenaphthylene, Acenaphthene, Phenanthrene, Fluoranthene, Benzo(b+j)fluoranthene, Benzo(a)pyrene, Benzo(k)fluoranthene, 3-Methylcholanthrene, Dibenz(a,h)acridine, Indeno(1,2,3-cd)pyrene, Dibenz(a,h)anthracene and Benzo(g,h,i)perylene. Also showed higher concentration of tested PAHs compared to the corresponding lowest concentration in the control sample, Naphthalene and Fluorene was 0.26±0.09, 0.24±0.06 and 0.14±0.07, 0.12±0.09 mg kg^{-1} in surface and subsurface soil sample respectively (Fig 6). Meanwhile, the mean concentrations of investigated PAHs as individual compounds in Murir burned forest; surface and subsurface soil sample are shown in Table 1 and Fig 5. The PAHs distributions in all the samples were dominated by Retene, Naphthalene, Acenaphthene, Acenaphthylene, Indeno(1,2,3-cd)pyrene, Benzo(a)pyrene, Fluorene, Fluoranthene, Benzo(b+j)fluoranthene, Benzo(k)fluoranthene, 3-Methylcholanthrene, Dibenz(a,h)acridine, Dibenz(a,h)anthracene, Benzo(g,h,i)perylene and Phenanthrene. Also showed a higher concentration of tested PAHs compared to the corresponding lowest concentration in the control sample, Naphthalene and Fluorene were~~as~~ 0.26±0.09, 0.24±0.06 and 0.14±0.07, 0.12±0.09 mg kg^{-1} in surface and subsurface soil sample respectively (Fig 6). Total of PAHs Concentration in Alsaqa, Murir and control soils were showed in Fig. 7. The distribution of the PAHs highest concentration in Alsaqa and Murir forests surface, subsurface and control soil showed in Fig. 8 and 9. Meanwhile, the distribution of the tested highest concentration of PAHs in Alsaqa and Murir forests surface, subsurface and control soil showed in Fig. 10 and 11. Retene distribution in Alsaqa and Murir forest surface, subsurface and control soils showed in Fig 12.

Table (4) Mean of PAHs concentration mg/kg^{-1} (ppm) in burned forests soils in Asir region.

PAHs	Alsaqa Forest		Murir Forest		Control	
	S	SS	S	SS	S	SS
Naphthalene	44.05±1.46	43.46±2.13	16.89±2.77	16.47±2.47	0.24±0.06	0.26±0.09
Acenaphthylene	35.88±2.37	34.11±2.45	15.11±2.41	13.69±3.22	ND	ND
Acenaphthene	35.02±1.48	33.41±2.26	14.89±2.29	16.30±2.03	ND	ND
Fluorene	37.14±4.12	36.21±3.58	13.22±2.36	15.43±2.55	0.12±0.09	0.14±0.07
Phenanthrene	35.23±2.39	34.58±2.44	12.48±2.37	12.83±1.37	ND	ND
Anthracene	33.89±2.52	33.35±2.59	13.77±2.97	14.52±2.41	ND	ND
Fluoranthene	29.99±3.17	29.31±2.48	14.61±3.30	16.44±2.66	ND	ND
Pyrene	37.91±2.09	36.43±2.25	13.88±2.12	14.37±1.29	ND	ND
Retene	57.28±3.56	55.47±4.15	28.83±3.35	25.59±4.31	ND	ND
Benzo(b+j)fluoranthene	32.48±2.81	28.80±2.24	12.82±2.40	15.39±1.98	ND	ND
Benzo(k)fluoranthene	29.31±2.11	27.18±2.05	14.10±2.10	14.80±2.12	ND	ND
Benzo(a)pyrene	29.88±3.27	27.48±2.88	14.68±1.38	16.59±2.20	ND	ND
3-Methylcholanthrene	34.24±2.44	33.18±2.27	14.72±2.04	16.71±2.15	ND	ND

Dibenz(a,h)acridine	28.26±2.57	26.39±2.37	13.40±2.18	14.64±3.31	ND	ND
Indeno(1,2,3-cd)pyrene	24.81±4.29	24.10±2.31	14.86±2.35	15.39±2.67	ND	ND
Dibenz(a,h)anthracene	26.97±3.31	24.30±2.71	13.77±3.31	14.52±2.29	ND	ND
Benzo(g,h,i)perylene	27.46±2.73	24.56±2.07	12.92±1.46	13.43±1.40	ND	ND
Total Σ PAHs	Σ 579.87	Σ 600.45	Σ 255.02	Σ 267.17	0.36±0.15	0.40±0.16

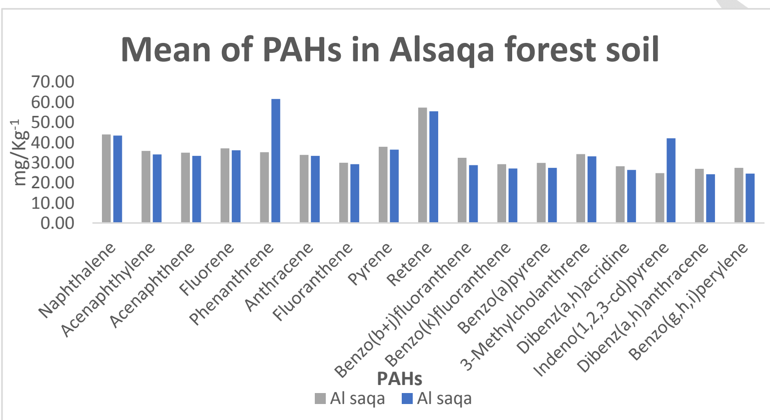


Figure (4) Average of PAHs concentration in Alsaqa forest soils

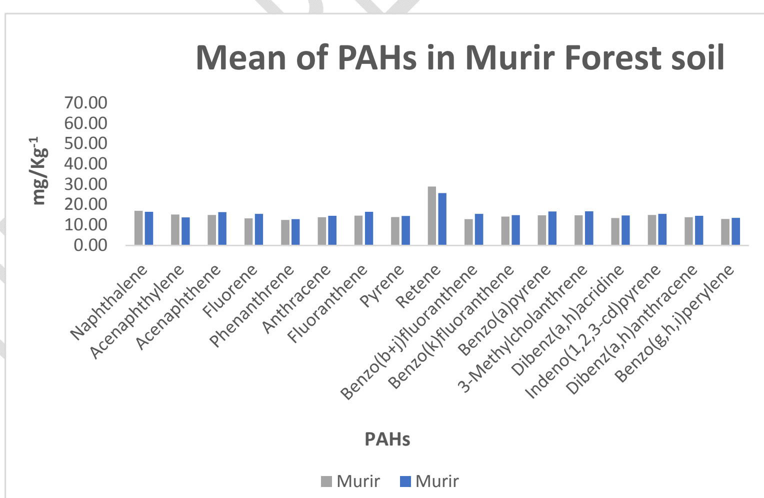


Figure (5) Average of PAHs concentration in Murir forest soils

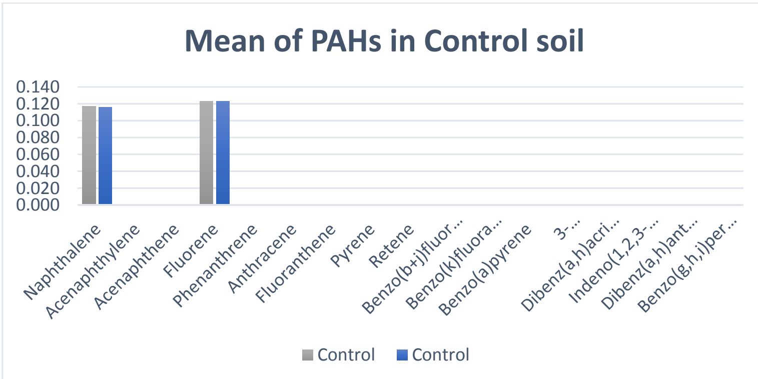


Figure (6) Average of PAHs concentration in control soils

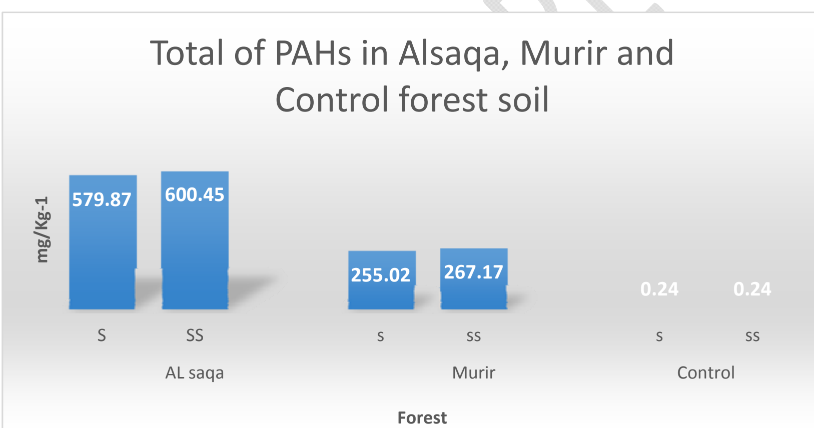


Figure (7) Total of PAHs Concentration in Alsaqa, Murir and control soils

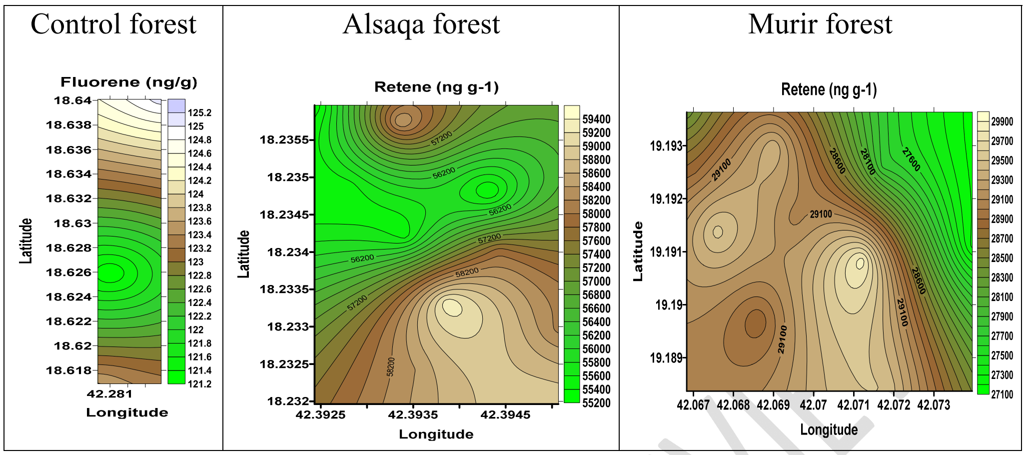


Figure (8) PAHs highest concentration in Alsaqa and Murir forests surface, and control soils.

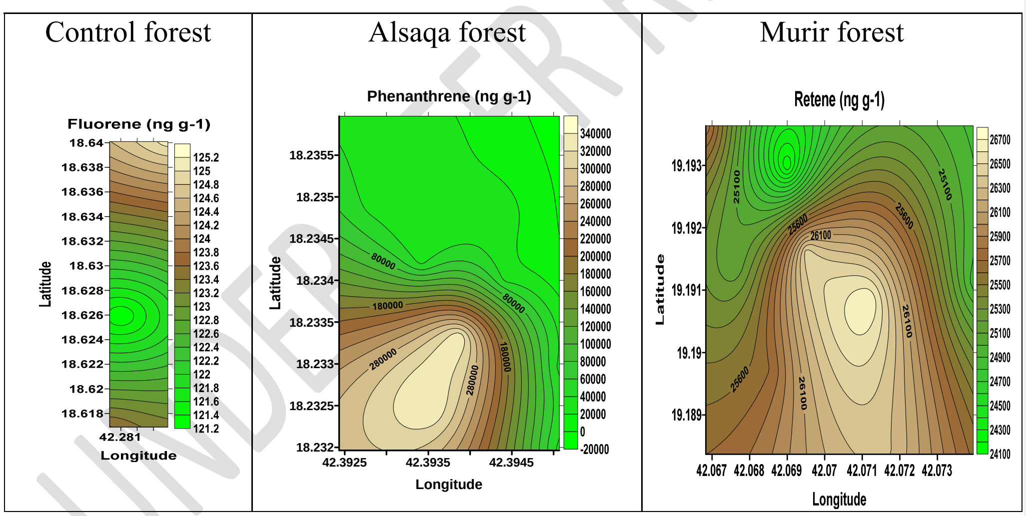


Figure (9)PAHs highest concentration in Alsaqa and Murir forests subsurface and control soils.

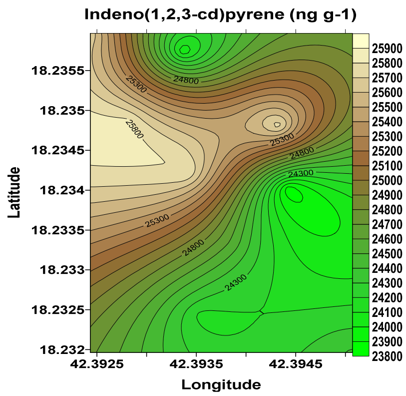
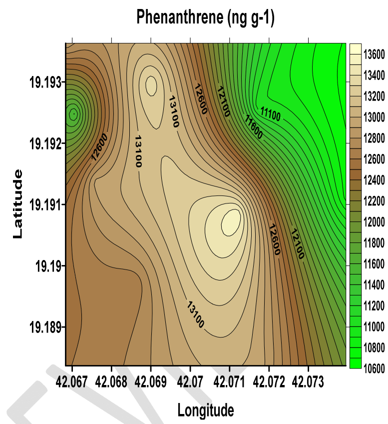
<table>
<tr><td>Control forest</td><td>Alsaqa forest</td><td>Murir forest</td></tr>
<tr><td>ND</td><td>
</td><td>
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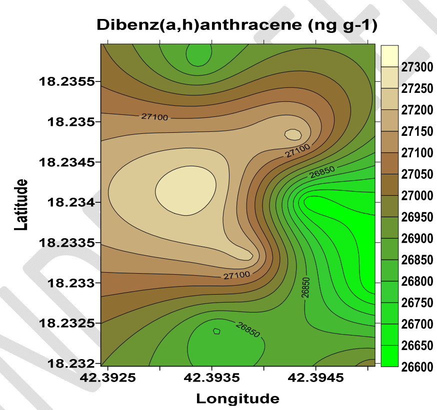
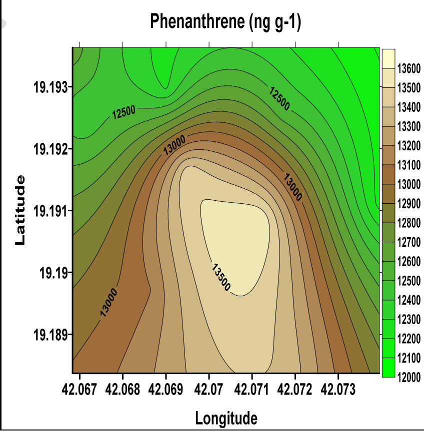
Figure (10)PAHs lowest concentration in Alsaqa and Murir forests surface, and control soils.

<table>
<tr><td>Control forest</td><td>Alsaqa forest</td><td>Murir forest</td></tr>
<tr><td>ND</td><td>
</td><td>
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</table>

Figure (11) PAHs lowest concentration in Alsaqa and Murir forests subsurface and control soils.

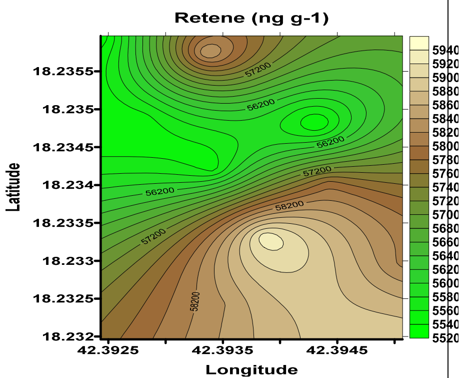
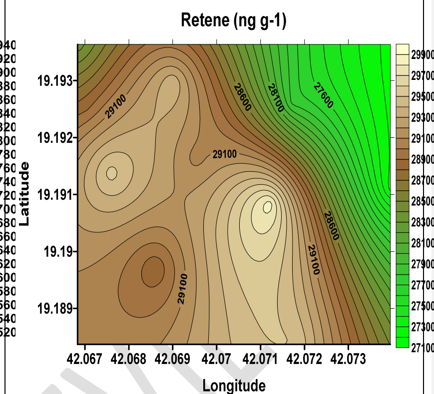
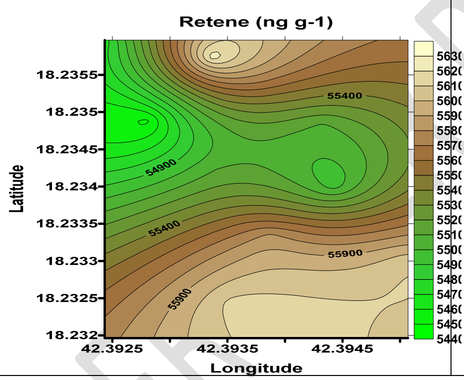
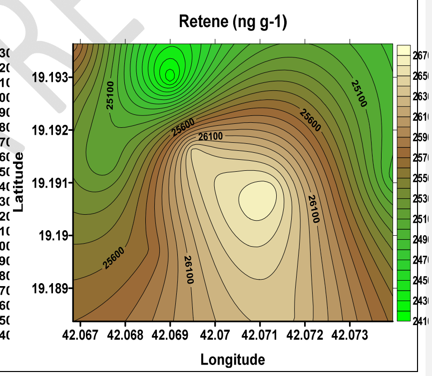
Control forest surface soils	Alsaqa forest surface soils	Murir forest surface soils
ND		
Control forest subsurface soils	**Alsaqa forest subsurface soils**	**Murir forest subsurface soils**
ND		

Figure (12) Retene Compound concentration in Alsaqa and Murir forest surface, subsurface and control soils.

Comparison of PAHs concentration in studied forest soil with Canadian soil quality guidelines.

The studied forest soils seem to pose serious adverse effects on human health, because the concentrations of the Phenanthrene, Dibenz(a,h)acridine, Benzo(k)fluoranthene, Benzo(b+j)fluoranthene and Naphthalene PAHs were higher the minimal concentrations listed under Canadian soil quality guidelines. On the other hand, the studied forest soils did not seem to pose any serious adverse effects on human health, because the concentrations of the Pyrene, Dibenz(a,h)acridine, Anthracene, Benzo(a)pyrene and Fluoranthene PAHs were below the minimal concentrations listed under Canadian soil quality guidelines as showed in Table (5). The present results in this research partially confirmed with **[10]** and Canadian soil quality guidelines 2008**[14]**.

Table (5): Comparison of the concentration of PAHs (mg/kg^{-1}) in forest soil with values listed by Canadian soil quality guidelines.

No	PAHs	Canadian Soil Quality (mgkg^{-1})					
		Agric.	Reside.	Comm.	Indus.	This Study	
						Alsaqa	Murir
1	Pyrene	0.1	10	100	100	37.17	14.25
2	Phenanthrene	0.046	0.046	0.046	0.046	34.84	12.65
3	Indeno(1,2,3-cd)pyrene	0.1	5	50	50	24.45	15.12
4	Dibenz(a,h)acridine	0.1	1	10	10	27.32	14.02
5	Benzo(k)fluoranthene	0.1	1	10	10	28.24	14.45
6	Benzo(b+j)fluoranthene	0.1	1	10	10	30.62	14.10
7	Anthracene	2.5	2.5	32	32	33.61	14.14
8	Benzo(a)pyrene	20	20	72	72	28.68	15.13
9	Fluoranthene	50	50	180	180	29.74	15.52
10	Naphthalene	0.013	0.013	0.013	0.013	43.75	16.68

Agric. =Agriculture, Reside. = Residential, Comm. = Commercial and Indus. = Industrial.

Conclusions

The wild fire in the current study forest soil that occasionally engulfed the forest believed to be responsible for the high level of tested PAHs comparing with soil control samples. Fire can lead~~s~~ to changes in the chemical properties of soil, particularly the quantity and quality of OM, availability of nutrients, CEC, and base saturation. The detected PAHs by applying the modified QuEChERS, and GCMSMSTQD method applied successfully for the extraction and determination of the 17 PAHs in burned forest soil samples. Retention time, LOD, LOQ, recovery % and a target mass of SRM scanning mode clearly reflect the developed and modified QuEChERS method offers an extraction efficient and easy sample preparation procedure for the determination 17 PAHs in soil samples investigated in this research. Recovery % ranged from 96.48±2.19 to 105.61±3.21%., the limit of detection (LOD) ranged from 3.71 to 6.77 µg kg^{-1}. M~~,~~ ~~m~~eanwhile the limit of quantification (LOQ) for the analyzed pesticides were in the range of 10.47 to 16.42 µg kg^{-1}. The concentrations of the investigated PAHs in Alsaqa forest surface (S) and subsurface (SS) soils ranged from 24.81±4.29 to 57.28±3.56 and 24.10±2.31to 55.47±4.15 mg kg^{-1}dry weight respectively. Meanwhile, the PAHs concertation in Murir surface and subsurface soils ranged from 12.48±2.37 to 28.83±3.35 and 12.83±1.37 to 25.59±4.31 mg kg^{-1}dry weight respectively. On the other hand, there is no detected PAHs except Naphthalene and Fluorene in an unburned control soil sample. The studied forest soils seems to pose serious adverse effects on human health, because the concentrations of the Phenanthrene, Dibenz(a,h)acridine, Benzo(k)fluoranthene, Benzo(b+j)fluoranthene and Naphthalene PAHs were higher the minimal concentrations listed under Canadian soil quality guidelines, and the rest of tested PAHs were below the minimal concentrations listed by the same Canadian soil quality guidelines.

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