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Removal of TPH, UCM, PAHs, and *Alk*-PAHs in oil-contaminated soil by thermal desorption

Byeongwook Choi[1], Sungjong Lee[1] and Eun Hea Jho[2*]

Abstract

Oil-contaminated soils from a former landfill and gas station site in Korea were treated by thermal desorption. The removal efficiencies of the different oil components such as total petroleum hydrocarbons (TPH), polyaromatic hydrocarbons (PAHs), unresolved complex mixtures (UCM), and alkylated PAHs (*Alk*-PAHs) by thermal desorption were determined. The effects of temperatures (200, 400, and 600 °C) and treatment times (15, 30, 45, and 60 min) on the thermal desorption efficiency were studied. The treatment efficiency increased with increasing temperature from 200 to 400 °C and with increasing treatment time. Almost complete removals of TPH, UCM, PAHs, and *Alk*-PAHs were observed after 15 min at 400 °C. The treatment temperatures of 400 and 600 °C did not show a significant difference (*p*-value > 0.05). Overall, this study shows that the different components of oil in the oil-contaminated soils can be treated effectively in a relatively short time by thermal desorption, and such high removal efficiency in a relatively short time for the oil-contaminated soils can be of advantage for the treatment of highly contaminated or weathered soils where biological treatment efficiency is low.

Keywords: Thermal desorption, Oil-contaminated soil, UCM, TPH, PAH

Introduction

Oil contamination of soil and groundwater due to various reasons including leaking pipes in industrial complexes and gas stations is regarded as serious environmental and social problems [1, 2]. Total petroleum hydrocarbons (TPH) are the main constituents of crude oil; thus, they are one of the most common pollutants found in oil-contaminated soils [3]. Polycyclic aromatic hydrocarbons (PAHs), which can also be found in oil-contaminated soils, are one of the crude oil components harmful to organisms. Structurally, PAHs have two or more fused aromatic rings with a pair of carbon atoms shared between rings in the molecules. They are often found in the atmospheric, soil, and water environments mostly due to anthropogenic activities [4]. They are not easily degraded in natural environment. PAHs have bioaccumulation potential, mutation potential, and carcinogenicity, hence they can be very harmful to living organisms [5]. PAHs can be alkylated and alkylated PAHs (*Alk*-PAHs) are more toxic than PAHs [6]. A large part of the hydrocarbons in crude oil cannot be identified and this part is referred to as unresolved complex mixture (UCM) hydrocarbons and UCM hydrocarbons are predominant in the environment, for example, in long-term weathered oil-contaminated soils, due to its resistance to natural weathering processes [7]. Previous study also reported toxic effects of UCM on benthic organisms [8]. However, studies reporting on the removal of UCM are very limited.

Remediation of oil-contaminated soils have often involved biological processes such as landfarming, bioremediation, and soil washing with surfactant-producing bacteria [9–11], but the remediation efficiency is relatively low and the treatment period is relatively long [12]. For example, in one previous study, the highest TPH removal rate of 80% was obtained after the biological treatment of an oil-contaminated soil by supplying microorganisms and various nutrients for 175 d [13].

*Correspondence: ejho001@jnu.ac.kr
[2] Department of Agricultural and Biological Chemistry, Chonnam National University, 77 Yongbong-ro, Buk-gu, Gwangju 61186, South Korea
Full list of author information is available at the end of the article

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Another study reported the TPH removal efficiency of 79% in the Kuwaiti oil-contaminated soil by the 16 d-sequential biowashing and biopile processes [11]. With PAHs, 89% removal of PAHs by biodegradation took 129 d [14]. Among various remediation techniques for oil-contaminated soils such as landfarming, soil washing, thermal desorption, and phytoremediation, thermal desorption can be one of the methods that has a relatively short treatment period [15]. Thermal desorption applies heat to contaminated soils, and oil components are removed via volatilization and/or desorption [16]. Thermal desorption has received increasing attention due to its advantages, such as suitability to different types of contaminants, short treatment period, high efficiency, high safety, and capability to recycle soil and contaminants [17].

Previous studies on thermal desorption of oil-contaminated soils focused on the optimization of treatment conditions such as temperature, flow rate of sweeping gas, and treatment time [17, 18]. Also, previous studies focused on the removal efficiencies of the target compound groups such as diesel [18]. Therefore, in this study, the changes in the different oil components found in oil-contaminated soils including TPH, PAHs, *Alk*-PAHs, and UCM were studied and compared under different conditions of thermal desorption. Specifically, a soil sample was taken from a site where it was used to be a landfill site from 1960 to 1970 and a gas station site from 1988 to 2010, and the thermal desorption efficiencies for removal of TPH, UCM, PAHs, and *Alk*-PAHs were determined. The effects of factors such as moisture content, temperature, and operating time on the thermal desorption efficiency were also studied.

Materials and methods
Soil characteristics
A soil sample taken from the site A where it was used to be a landfill site followed by a gas station site were air-dried and sieved through a 2 mm sieve. The soil sample was placed at 4 °C until being used in the experiments. The soil texture was sandy clay loam with 66% sand, 20% clay, and 14% silt. The water holing capacity (WHC) was $43 \pm 0.004\%$, and pH was 6.99 ± 0.02. The background TPH, UCM, PAHs, and *Alk*-PAHs concentrations were 1965 ± 16, 1441 ± 9, 0.76 ± 0.02, and 61 ± 2.1 mg kg^{-1}, respectively.

Thermal desorption experiments
The thermal desorption was carried out in a muffle furnace (DMF-3 T, Lab House, Korea). Different temperatures (200, 400, 600 °C) and different operation times (15, 30, 45, 60 min) were used to run the thermal desorption experiments. For each sample, 10 g of soil were put in

a ceramic plate, which was placed in the furnace. After treatment, the soil samples were removed from the furnace, and cooled down in a desiccator. All these experiments were conducted in triplicate under each condition. The removal efficiency (R_e) was calculated by using Eq. 1.

$$R_e(\%) = (C_0 - C/C_0) \times 100 \tag{1}$$

where C_0 is the initial contaminant concentration in soil (mg kg^{-1}) and C is the residual concentration of contaminant in soil after the thermal treatment (mg kg^{-1}).
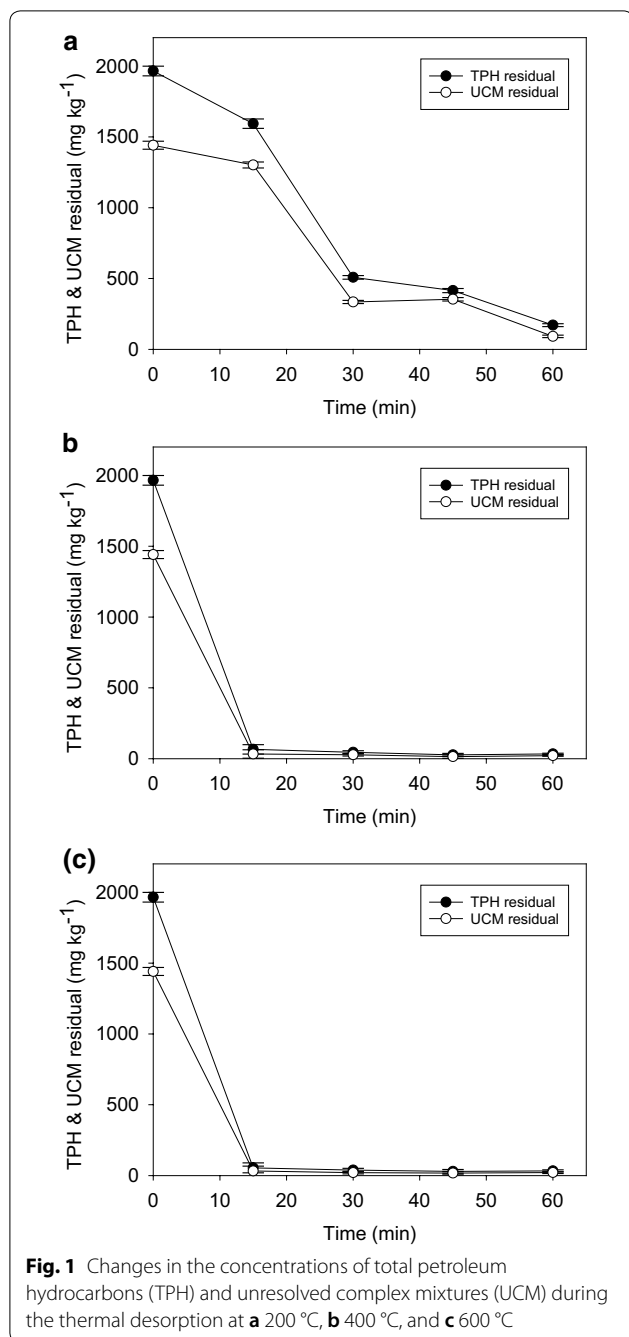
Analysis of TPH, UCM, PAHs, and *Alk*-PAHs
Extraction and purification of the soil samples were carried out according to the method of quantitative oil analysis method [19]. TPH, UCM, PAHs, and *Alk*-PAHs were extracted with *n*-hexane (95%, J. T. Baker) using a Soxhlet apparatus for 16 h. The residual TPH and UCM concentrations in the extracts were analyzed using a gas chromatograph equipped with a flame ionization detector (GC-FID; Agilent 6890 N, Agilent, DE, USA) with split mode (1:10) injection on a bonded phase fused silica capillary column DB-5 (Agilent J&W, 30 m × 0.25 mm i.d. × 0.25 μm film thickness). The column temperature was kept at 40 °C for 8 min, and ramped at 12 °C min^{-1} to 320 °C, which was held for 20 min. The injector and detector temperatures were kept at 250 and 320 °C, respectively. The flow rate of N$_2$ was 1 mL min^{-1}. The residual concentrations of PAHs and *Alk*-PAHs in the extracts were analyzed using gas chromatograph equipped with a mass spectrometry (GC–MS; Agilent 6890/HP 5973, Agilent, DE, USA) with split mode (1:10) injection on a bonded phase fused silica capillary column HP-5MS Ultra Inert (30 m × 0.25 mm i.d. × 0.25 um film thickness). The column temperature was 60 °C for 6 min, and ramped at 6 °C min^{-1} to 300 °C, which was held for 13 min. The injector and detector temperatures were kept at 260 and 300 °C, respectively. The flow rate of He was 1 mL min^{-1}. For TPH analysis, the surrogate standard of o-terphenyl and the internal standard of 5α-androstane were used. For the analysis of PAHs and *Alk*-PAHs, dibenzothiophene-D8 and PAHs internal standard 5 mix (naphthalene-D8, acenaphthene-D10, phenanthrene-D10, chrysene-D12, perylene-D12) were used as the surrogate standards, and *p*-terphenyl-D14 was used as the internal standard. The standards were purchased from the Accustandard.
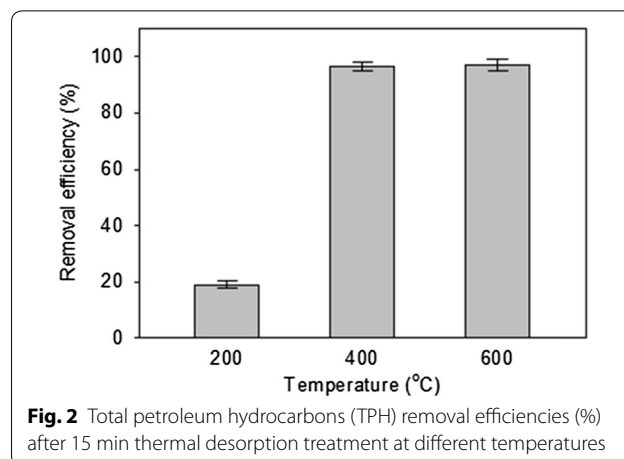
Results and discussion
Removal of TPH and UCM
The changes in the residual concentrations of TPH and UCM during the thermal desorption at 200 °C are shown in Fig. 1a. The concentrations of TPH and UCM gradually decreased with time reaching the average removal

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Fig. 1 Changes in the concentrations of total petroleum hydrocarbons (TPH) and unresolved complex mixtures (UCM) during the thermal desorption at **a** 200 °C, **b** 400 °C, and **c** 600 °C

Fig. 2 Total petroleum hydrocarbons (TPH) removal efficiencies (%) after 15 min thermal desorption treatment at different temperatures

were statistically similar at 400 and 600 °C (p-value > 0.05) (Fig. 2). The maximum TPH removal efficiency of 99% was obtained at 400 and 600 °C after 15 min treatment (Fig. 2). Similarly, previous studies reported comparable TPH removal efficiencies. One previous study reported 94.7% of TPH removal after 15 min thermal desorption of petroleum oil-contaminated soil (initial concentration of 5133 ± 508 mg kg^{-1}) at 200 °C in a rotary kiln [20]. In another study, the maximum TPH removal efficiency of about 98% was achieved at 500 °C after 15 min treatment of the combined microwave and thermal desorption processes [21].

Thermal desorption can be classified as low temperature thermal desorption or high temperature thermal desorption, and the remedial process includes the heating (direct or indirect) of the contaminated environmental matrix at an appropriate temperature in a vacuum or carrier gas system to separate target volatile or semi-volatile contaminants from the matrix [22]. In thermal desorption, the boundary between high and low temperatures is not clear, but it is classified as around 300–350 °C. However, very high heating temperatures destroy the soil structure, volatilize and pyrolyze organic matter in the soil, and decompose carbonates in soil minerals, and this makes inappropriate to reuse soil after contaminant treatment and/or subsequent reclamation [23].

Figure 3 shows the GC chromatograms of the TPH and UCM. The UCM is shown as humps in the GC chromatograms [7]. In a previous study, the GC-resolved peaks of the GC chromatograms were used to determine the total GC detectable TPH, GC-resolved peaks, and UCM [24]. In the case of the raw soil sample (i.e., untreated soil sample), the amount of UCM (i.e., the area under the hump) was found to be considerably high (43% of the total oil content). After thermal treatment at 200 °C for 30 and 60 min, the areas under the UCM chromatograms
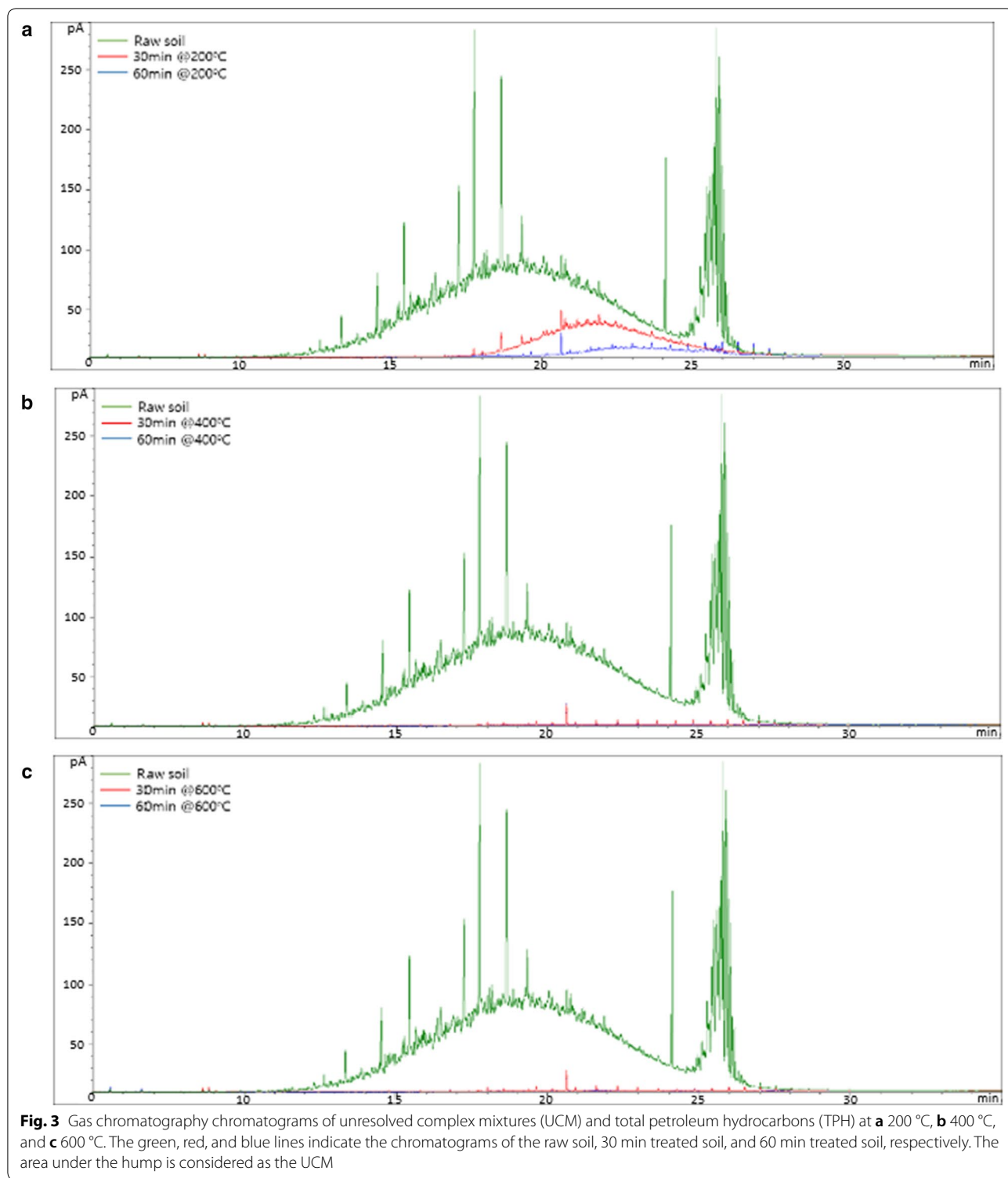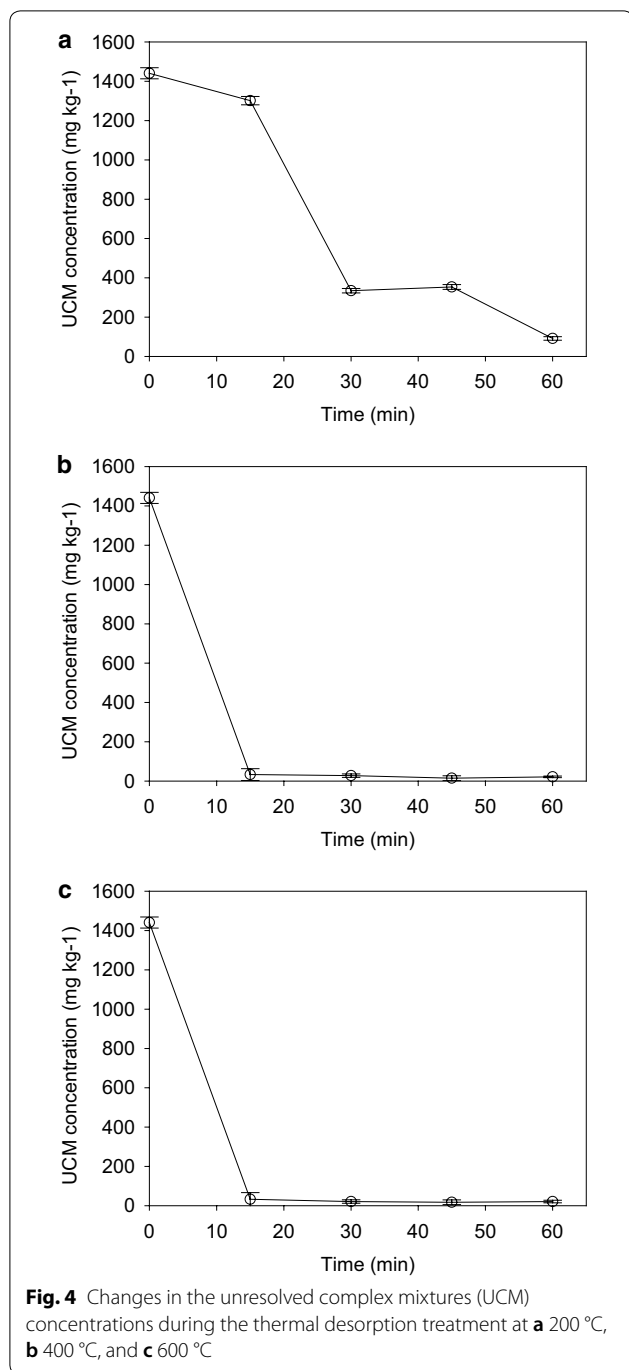
efficiencies of 74 and 76%, respectively, after 30 min treatment. After 60 min treatment, the average removal efficiencies increased to 92% for TPH and 94% for UCM. Similar trends were observed at 400 and 600 °C (Fig. 1b, c). At both temperatures, almost complete removal was achieved after 15 min treatment. When the removal efficiencies after 15 min treatment at different temperatures are compared, the removal efficiency was lower at 200 °C than at higher temperatures, but the removal efficiencies

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Fig. 3 Gas chromatography chromatograms of unresolved complex mixtures (UCM) and total petroleum hydrocarbons (TPH) at **a** 200 °C, **b** 400 °C, and **c** 600 °C. The green, red, and blue lines indicate the chromatograms of the raw soil, 30 min treated soil, and 60 min treated soil, respectively. The area under the hump is considered as the UCM

were remarkably reduced (Fig. 3a), and similar reduction in the areas under the UCM chromatograms with treatment time was also observed at 400 and 600 °C (Fig. 3b, c). The changes in the UCM concentrations are shown in Fig. 4. The removal was slower at 200 °C than at higher temperatures (Fig. 4). Almost complete UCM removal was observed after 15 min treatment at 400 and 600 °C (Fig. 4). The removal did not show a statistically

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Fig. 4 Changes in the unresolved complex mixtures (UCM) concentrations during the thermal desorption treatment at **a** 200 ℃, **b** 400 ℃, and **c** 600 ℃

Fig. 5 Changes in the concentrations of **a** polyaromatic hydrocarbons (PAHs) and **b** alkylated polyaromatic hydrocarbons (*Alk*-PAHs) in the oil-contaminated soil during the thermal desorption treatment at different concentrations

significant difference between the treatment temperatures of 400 and 600 ℃ (*p*-value > 0.05). Recent studies on UCM tried to analyze the UCM hydrocarbons and investigated the biodegradation potential of UCM hydrocarbons [24, 25]. Also, a reduction in UCM was observed during the bioremediation of PAHs-contaminated soil [26]. However, studies on UCM removal from oil-contaminated soils are limited.
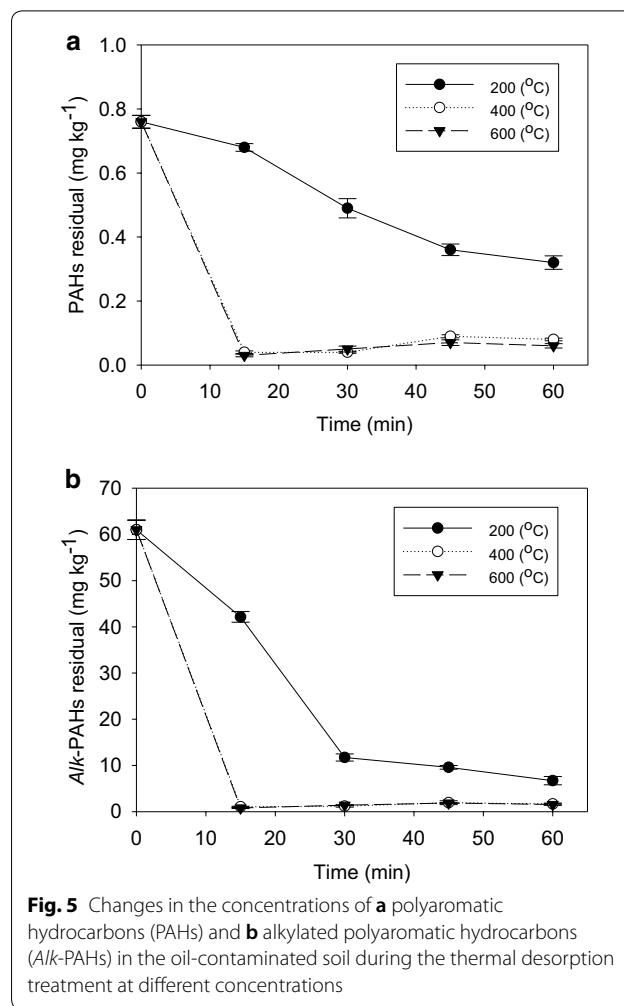
Removal of PAHs and *Alk*-PAHs

The changes in the PAHs and *Alk*-PAHs concentrations during the thermal desorption treatment at different temperatures are shown in Fig. 5. The initial PAHs concentration was a trace amount (1.2% of the total oil content) compared to other components (e.g., TPH, UCM). The removal efficiency of PAHs increased with increasing temperature from 200 to 400 ℃, but no further increase was observed with further increase in temperature to 600 ℃ (Fig. 5a). For example, after 15 min treatment, the average removal efficiencies were 32, 96, and 97% at 200, 400, and 600 ℃, respectively. *Alk*-PAHs were reduced by 39% to 42 mg kg^{-1} after 15 min treatment at 200 ℃, and by 90% to 6.7 mg kg^{-1} after 60 min treatment at 200 ℃ (Fig. 5b). At 400 ℃, 98% was removed after 15 min treatment, while 99% was removed after 15 min treatment at 600 ℃. Previous study showed similarly high PAHs removal at higher temperatures. For example, when PAHs were removed using thermal incineration at temperatures from 870 to 1200 ℃, the removal efficiency

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was > 90%, and the removal of PAHs using an indirect heating type thermal desorption device at a temperature of > 450 °C showed 99.9% removal efficiency after 1 h [27].

Author details
[1] Department of Environmental Science, Hankuk University of Foreign Studies, 81 Oedae-ro, Mohyeon-eup, Cheoin-gu, Yongin-si, Gyeonggi 17035, South Korea. [2] Department of Agricultural and Biological Chemistry, Chonnam National University, 77 Yongbong-ro, Buk-gu, Gwangju 61186, South Korea.

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