# Identification of weathered multiple petroleum products in contaminated soils by characterizing unresolved complex mixture hump in gas chromatograph data

Soo-Kyung Jeon [a,b], Dongwook Kwon [a], Seunghak Lee [a,b,*]

[a] Center for Water Resource Cycle, Green City Technology Institute, Korea Institute of Science and Technology (KIST), Seoul 136-792, Republic of Korea
[b] Energy Environment Policy and Technology, Green School, Korea University(KU) - Korea Institute of Science and Technology (KIST), Seoul 136-701, Republic of Korea

## HIGHLIGHTS

- Unresolved complex mixture (UCM) hump was observed only in soils containing petroleum
- Soils containing kerosene/diesel/lubricating oil have specific UCM signatures
- UCM signatures survived environmental weathering of contaminated soils
- UCM hump method distinguished individual products in soil containing multiple contaminants

## GRAPHICAL ABSTRACT
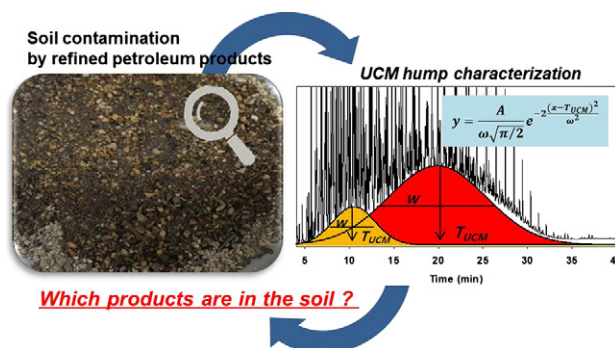


## ARTICLE INFO

## ABSTRACT

A new method for identifying the petroleum products in contaminated soils is presented, which characterizes the unresolved complex mixture (UCM) hump in the baseline of gas chromatograph (GC) data. The UCM hump identified in soil data was fitted to the *Gaussian* function, and characterized according to the time for the maximum point ($T_{UCM}$) and the width of the hump ($w$). Experimental results showed that a UCM hump should be clearly observed in soils when contaminated with petroleum, and that soils contaminated with kerosene, diesel, or some lubricating oils estimated herein should present different characteristic values of $T_{UCM}$ and $w$. Even though the environmental weathering of contaminated soils under evaporative conditions might cause variations in these characteristic values, they converged to specific constants depending on the product. The method could also differentiate between multiple petroleum contaminants in soil. Feasibility was evaluated using soils from a military oil storage site that was closed in 1970. The soil contaminants identified by the proposed method corresponded to the historical storage records, suggesting that the UCM hump characterization method could have strong potential in environmental forensics for differentiating products in petroleum-contaminated soils.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

With rapid industrialization, soil pollution by refined petroleum products such as gasoline, kerosene, diesel, and lubricating oil has been frequently reported, requiring appropriate measures to counteract

* Corresponding author.
  E-mail address: seunglee@kist.re.kr (S. Lee).

their harmful effects on ecology and human health (Wang and Fingas, 2003). Prior to remedial action, identification of the contaminant source is essential for determining the responsible party and delineating the extent of remediation (Wang et al., 2006). Environmental forensics for petroleum hydrocarbons has been studied since the late 1970s (Bentz, 1978; Albaiges and Albrecht, 1979), however, most previous studies focused on marine contamination by crude oils containing a variety of environmentally persistent biomarkers readily available for source identification (Kvenvolden et al., 1995; Kaplan et al., 1997; Peters et al., 2005). For petroleum products, however, most biomarkers are removed during the refining process, which makes their identification from environmental samples highly challenging. The conventional practice of simply comparing the similarities in gas chromatography (GC) peak patterns between the suspect oil and the samples is known to include crucial errors in identifying the petroleum species, because the GC peaks of a sample can be significantly altered by environmental weathering. Even those compounds suggested as potential fingerprints for refined petroleum products (e.g., sesquiterpenes, polycyclic aromatic hydrocarbons, $C_3$-alkylbenzenes, etc.) (Alimi et al., 2003; da Silva and Bícego, 2010) are still prone to damage in the subsurface environment (Head et al., 2003; Jones et al., 2008; Hallmann et al., 2008), which emphasizes the necessity of developing more reliable identification indices or methods.

Unresolved complex mixture (UCM) refers to the unseparated hydrocarbon fractions in analyzing petroleum-affected samples via GC, which is shown as a hump in the GC baseline data (Gough and Rowland, 1990; Wang et al., 1999; Frysinger et al., 2003; Booth et al., 2007). This hump in the data consists of an estimated 250,000 compounds, including alkanes, branched alkanes, cycloalkanes, monoaromatics, multi-ring aromatics, hetero-atomics, steranes, and cyclic triterpenoids (Frysinger et al., 2003; Sutton et al., 2005; Ventura et al., 2008). In particular, previous researchers recognized that the UCM hump in GC data was clearly observed even after long-term weathering had eliminated most of the peaks for normal and branched alkanes in the GC data (Head et al., 2003; Hallmann et al., 2008; Reddy et al., 2002).

In this study, we proposed and estimated the UCM hump in GC data as a potential index for identifying multiple weathered petroleum products in contaminated soils. Previous studies suggested UCM as evidence for petroleum contamination in soils (Asia et al., 2009; Rouidi et al., 2013). In addition, several researchers have reported that the retention time ranges of $n$-alkanes and UCM in GC data might vary depending on the oil type (i.e., gasoline, jet fuel, diesel, heavy fuel oil, and lubricating oil) (Wang and Fingas, 2003; Wang and Stout, 2010). However, no approach for distinguishing the petroleum products in contaminated soils has been proposed to date. To the best of our knowledge, this is the first study to present a systematic method for utilizing the shape of a UCM hump as a fingerprint for identifying petroleum products in soils. For quantitative characterization, a UCM hump was fitted to the formulaic *Gaussian* function based on its bell-like shape, and the time for the maximum point ($T_{UCM}$) and the width ($w$) of the hump were defined as characteristic values. The use of the UCM hump as a fingerprint was evaluated by comparing $T_{UCM}$ and $w$ observed in soils that were artificially contaminated with a single petroleum product (i.e., kerosene, diesel, or lubricating oil), and examining any possible contribution of soil organic matter to the shape of the UCM hump. In order to estimate the influence of environmental weathering, variations in $T_{UCM}$ and $w$ in the artificially contaminated soils were monitored for a year following exposure to atmospheric conditions. The applicability of UCM hump characterization for discriminating between multiple contaminants was evaluated using soils that were artificially contaminated with various petroleum mixtures. Finally, the feasibility of the proposed method was verified using highly weathered petroleum-contaminated soils obtained from a former oil storage depot.

## 2. Materials and methods

### 2.1. Materials

Different gasolines, kerosenes, diesels, and lubricating oils were purchased from four oil-refining companies in Korea. Specifically, lubricating oils include SAE 5W-30 KIXX PAO (GS-Caltex, Korea), SAE 5W-30 (SK lubricants, Korea), SAE 5W-30 gold (S-oil, Korea), and API CH-4 ACEA B3/B4 SAE 5W-30 (HYUNDAI MOBIS, Korea). All chemicals used in the experiments were of reagent grade, including acetone (≥99.4%, JT Baker, PA, USA), dichloromethane (DCM, ≥ 99.0%; JT Baker), and sodium sulfate ($Na_2SO_4$, ≥99.0%, Sigma-Aldrich, MO, USA). Soils used in the laboratory experiments were collected from a hill at the Korea Institute of Science and Technology, and used after drying in air for 24 h and passing through a No. 10 sieve (<2 mm). Commercial humus and the soils collected from a flower garden and an orchard in suburban Seoul were used for estimating the influence of soil organic matter on the shape of the UCM hump. Petroleum-contaminated field soils were obtained from a military oil storage site that closed in 1970.

### 2.2. Laboratory experiments using artificially petroleum-contaminated soils

Petroleum-contaminated soils were simulated by manually mixing 100 g of soil with 1.0 g of a single petroleum product or with petroleum mixtures. Petroleum mixtures of two products (i.e., kerosene:diesel, kerosene:lubricating oil, and diesel:lubricating oil) were prepared at ratios of 1:1, 1:2, 1:4, and 1:9, and the three product mixtures (i.e., kerosene:diesel:lubricating oil) at 1:1:1, 1:1:3, 1:3:1, and 3:1:1 by volume (Table S1). For estimating weathering effects, the petroleum-contaminated soils were kept in a room equipped with a fume hood while collecting about 3.5 g soil samples from three different locations (totally 10.5 g) and analyzing their UCM humps at predetermined time intervals for a year. The average temperature and humidity of the room exposed to the sunlight was 25 °C and 35%, respectively. All experiments were performed in triplicate, and the results presented here are the mean of the three experiments ± standard deviation.

### 2.3. Analytical methods

Extracts from the soil samples for GC analysis were prepared by: 1) mixing 10 g of soil with 10 ml of DCM and 1 mg of $Na_2SO_4$ in a 50 ml amber vial; 2) shaking the vial on a rotary shaker (JWS-100; Jeniewell, Korea) at 40 rpm for 2 h; and 3) filtering through a 0.45 μm PTFE filter (Cat. No. 6784-1304; Whatman, UK).

The prepared samples were analyzed using a gas chromatograph equipped with a flame ionization detector (GC-FID, HP 6890N; Agilent Technologies, CA, USA) and an auto sampler (7683; Agilent Technologies). A DB-5 capillary column (30 m × 0.32 mm i.d., 0.5 μm film thickness, 19091J-113; Agilent Technologies) was used, and nitrogen ($N_2$) was used as the carrier gas (flow 1.0 ml/min). The split ratio was 1 to 10. The injector and detector temperatures were 300 and 320 °C, respectively. The oven temperature was set at 50 °C for 2 min, increased to 320 °C at 8 °C/min, and then held for 20 min.

The extraction and analytical methods herein are not valid for quantifying the complete fractions of UCM, including, for example, naphthenic acids, in petroleum despite their effectiveness for the non-polar fractions.

### 2.4. Characterization of the UCM hump in GC data

Based on its symmetric bell-like shape, a single UCM hump was described via a *Gaussian* distribution. For this, the coordinates of the UCM were generated by applying the moving average for the coordinates of each 10,000 points in the GC data. Then, the UCM coordinates were fitted into a *Gaussian* function, or the superposition of multiple *Gaussian*