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PART VI: Environmental Forensics

Chapter 13

THE CASE ON ASSESSMENT OF SPILLED OIL WITH MIXED FREE PRODUCT IN SEOUL

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ABSTRACT

The purpose of this study is to assess sources of contamination by analyzing the free product and oil compounds in groundwater near the Subway Station, located adjacent to the Yongsan Garrison in Seoul, Republic of Korea. All of the samples collected twice were groundwater and free product in a monitoring well. Analysis items are TPH fingerprinting, pristane/phytane ratio, alkylbenzene pattern, PAH&alkyl PAH, antioxidant, icing inhibitor, PIANO, element(C, N, H), and sulfur. Using ratio of pristane/phytane, we were able to distinguished fuel type between kerosene and JP-8 samples, which was impossible by GC/FID pattern. Alkyl benzene pattern was very effective in distinguishing between JP-8 and kerosene. It is very important that 2,4-dimethyl-6-tert-butyl phenol, an antioxidant used only for JP-8, was detected in free product samples. The concentration of sulfur in kerosene fuel is much lower than that of JP-8, and the total contents of sulfur in environmental samples can be used to differentiate the fuel type of spilled oil between kerosene and JP-8. In conclusion, according to the result of a variety of analytical methods to find the source of spilled fuel, it had been found that the fuel type detected in the tunnel of subway station and monitoring wells outside of Yongsan Garrison and the monitoring wells inside of Yongsan Garrison are the same.

Keywords: Oil; Free product; groundwater; alkylbenzene; sulfur

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1. INTRODUCTION

The Noksapyong Subway site is located north of the Yongsan Garrison, in the city of Seoul, ROK. The investigation area includes approximately 50,000 square meters of paved ground, wooded ground, and sloped terrain that extends from the AAFES Gas Station to Noksapyong Subway Station.

Construction on the Noksapyong segment of Subway Line Number 6 began in December 1995 and was completed in July 2000. In January 2001, the free product was found in seepage water within the Noksapyong Subway tunnels, located to the northwest of the army garrison in Seoul, Korea. The service station within the army garrison has been in use since 1974 when the underground storage tanks (USTs) were installed. In 1990, water was observed in premium gasoline tanks and the tanks were replaced. In July 2000, the use of the premium fuel line was suspended when the line failed a routine pressure test. The fuel line was subsequently replaced in January 2001.

In February 2001, two USTs located within the Housing Area failed leak tests and were subsequently removed and replaced with aboveground storage tanks (ASTs). The tanks at these locations are used to store diesel or JP-8 fuel for heating purposes. After an additional leak test was performed on USTs near the Service Station area, a UST was also removed from the area immediately adjacent to the Military Dog Training Ground in August 2001. This UST purportedly contained kerosene for heating purpose(Samsung, 2002).

The U.S. forces in Korea (USFK) and the Seoul City (SC) have been confused over the source of the fuel contamination near Noksapyong Subway Station. The fuel type was found to be gasoline and kerosene. The USFK recognized that the gasoline was from the Yongsan Garrison but not the kerosene. This led to reinvestigation of the source for identifying the kerosene.

To confirm the source of the contamination, the type of fuel in the contaminated area should be identical to the potential source of the contamination. A simple pattern analysis of hydrocarbon cannot provide the answer. Fuel is a quite complicated compound ranging from a simple straight chain-type saturated hydrocarbon (n-alkane), unsaturated hydrocarbon and aromatic hydrocarbon, etc. Once exposed to the environment, oil undergoes various chemical processes including volatilization, dissolution, microbial or chemical decomposition, which drastically transforms the saturated hydrocarbon. This makes it impossible to accurately identify the type of fuel with the simple hydrocarbon pattern analysis.

In particular, as for the one at the center of controversy, kerosene, most oil refineries in Korea use a similar-quality crude oil; the fuel used at the U.S. Army base has been also supplied from a Korean refinery, which makes it very difficult to identify the source of contamination. But it is believed that a very thorough and detailed analysis of the chemical features of the oil could identify the subtle difference between oil types. This will enable us to identify the source of contamination. Most oil goes through volatilization, dissolution and microbial or photochemical decomposition processes but the compounds which were not transformed can be utilized as a very important marker. Therefore development of the most reliable and accurate analytical method is essential.

Required is a method that allows the most reliable and accurate analysis. Especially, the pattern analysis of the difficult-to-decompose contained in the oil can be used as a very useful index to distinguish the oil type and analysis of additives added for different purposes can provide a clue to determine the source of contamination.

The USFK recognized that the gasoline component in the contaminated groundwater at Noksapyong Station tunnel came from the Yongsan Garrison but not for Kerosene. Therefore, this research is to identify the source of contamination by analyzing the free product and groundwater samples near the Noksapyong station and tunnel.

2. MATERIALS AND METHODS

2.1 Sample Collection and Analysis Items

Commercial gasoline, white kerosene, boiler kerosene and diesel control standard samples were taken from LG and SK gas stations near the Noksapyong station. At the same time, gasoline, kerosene and diesel control standard samples were taken from the AAFES gas station located within the Yongsan Garrison and two JP-8s from the AST, and they are used as a reference.

All of the samples collected twice jointly by SC and USFK were ground water and free product and its details are as follows: Analysis items are: TPH fingerprinting, TPH (gasoline and kerosene), pristane/phytane ratio, BTEX, alkylbenzene pattern, PAH & Alkyl PAH, PIANO, element (C,N,H), sulfur, antioxidant and icing inhibitor. It was attempted to identify the contamination source by analyzing each item using the best possible analytical method for them and combining all the findings.

When it comes to the groundwater samples, SC and USFK team together gathered in the following order: anti-oxidant, icing inhibitor, biomarker (alkylbenzene included), TPH fingerprinting (gasoline, kerosene included), and stable isotopes.

The first-phase samples were collected from November 21, 2002 to November 26, 2002 and the groundwater samples taken from 12 wells near New Veterinary Clinic in Yongsan Garrison (NVC) (B01-729, B01-730, B01-788, B01-868, B01-869, B01-870, B01-874, B01-875, B01-877, B01-880, RW02-103, and RW02-106) and from 8 wells on monitoring well installed by the Seoul City(MSC) (BH-1 to 8), and from 8 spots within the Noksapyong Station tunnel(20K-187C, 20K-230C, 20K-217C, 20K-230C, 20K-246C, 20K-260C, and 20K-525C). Two samples were taken from BH-7 and 20K-187C as duplicate sample. The free product samples were taken from 8 monitoring wells where free product was accumulated (NVC: B01-730, B01-868, B01-874, B01-880 and MSC near Noksapyong station (BH-5, BH-6, BH-7), and 19K-890 in the direction of Itaewon from the south tunnel of Noksapyong station. Twelve samples were taken from four locations on November 22 as fuel control standard (ASTs-1 near 52nd Medical Battalion; ASTs -2 in front of the building S4348 within the housing area; premium gasoline, regular gasoline, kerosene, diesel at AAFES gas station, white kerosene, boiler kerosene from

SK Namkyung gas station and LG Daesung gas station). As a result, there were a total 30 groundwater samples (duplicates included), 8 free product samples, 5 soil samples and 12 reference samples for the first-phase underground sample collection.

In the second phase, samples were collected from February 14, 2003 and February 24 throughout 26, 2003. On February 22 Korea and U.S.A. jointly collected samples on 10 locations inside the underground tunnels of Noksapyong station (20K-187C, 20K-230C, 20K-217S,

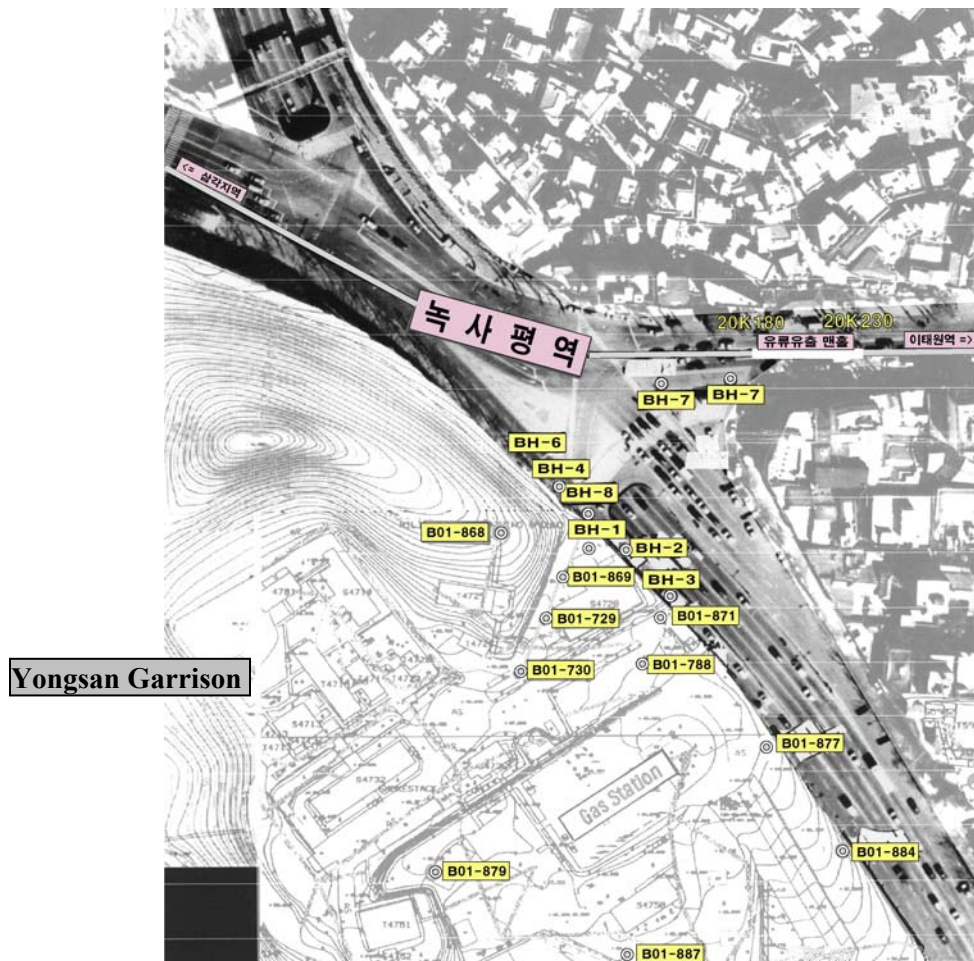


Figure 1. Site map near Noksapyong Subway Station

20K- 230S, 20K-246S, 20K-260C, 20K-525C, BH-32, BH-33) and three locations on the 19K area (19K-810C, 19K-755C, 19K-550C) and on February 24 on 20 MSC on the outer track of NVC (BH-1 to 16, BH-18 to 21), on February 25 on 13 locations within the USFK base near NVC (B01-729, B01-788, B01-868, B01-869, B01-870, B01-874, B01-875, B01-877, B01-880, RW02-103, RW02-106, RW02-107, RW02-108). Four fuel control standards were collected on two spots on February 25 (ASTS: JP-8, gas station: premium gasoline, regular gasoline,

kerosene) and for duplicates two samples were picked per item on BH-6, B01-874, B01-880 and 20K-260S. Free fuel control standards were taken from eight monitoring wells (monitoring well near NVC: B01-788, B01- 874, B01-877, B01-880 and monitoring wells for Korean side on outer block of NVC: BH-5, BH-6, BH-7 and 19K-890 in the direction of Itaewon from the south tunnel of Noksapyong station). Therefore, the total number of groundwater samples collected in the second phase was 61 including duplicate samples, along with 8 free product samples and 4 reference fuel control standards. Fig 1 is Site map near Noksapyong Subway Station.

Samples were collected using the disposable, bottom discharging bailer (ASTM D4489) and it was transferred into the newly purchased clean brown-colored 1000 ml(1L) glass bottle along with the Teflon-coated cap without washing them. Free product samples were contained in the newly purchased clean brown-colored 500 ml glass bottle (or 40 ml to 1ml VOC bottle, size varies depending on the quantity of the oil collected) along with the Teflon-coated cap without washing them.

Those samples were stored in a dark area in the temperature of 4-5°C and pretreatment was made within 7 days and then analysis was completed within 30 days (ASTM D3325).

2.2 Chemicals and Analysis Methods

The methylene chloride used for this study was solvent used for analyzing residual agricultural chemicals produced by Merck and standard materials were purchased from Aldrich or Sigma. Other reagents were used special reagents whose seal is not broken.

Sodium sulfate (Na₂SO₄, Kanto, Japan, for pesticide residue) were used as reagents. Water was purified in milli-Q (Millipore Corp., Milford, MA). Table 1 shows methods for analysis of free product and groundwater samples.

3. RESULTS AND DISCUSSION

3.1 TPH pattern and pristane/phytane

Unknown oil component show different patterns depending on oil type and origin. n-alkanes and isoprenoids of saturated hydrocarbon are feeble in toxicity; however, they are the components that are used very often as a tracing material in spilled oil because they are the primary component. GC-FID chromatogram shows the pattern of these n-alkanes and isoprenoids. They have specific fingerprint in accordance with petroleum hydrocarbon type. However, environmentally contaminated oil changes its pattern by weathering, distribution between phases and vaporation(Wang, Z 1995).

GC-FID chromatograms were obtained by analyzing water phase and free product according to each analysis method after distributing fuel control standard sample of LG, SK, GS and ASTs into groundwater that is not contaminated with oil for a certain amount of time. If we compare

Table 1. Method for Analyses of Free Product and Groundwater Sample

Items	Free Product		Ground Water	
	Pre	Method	Pre	Method
TPH Fingerprinting	EPA 3580	EPA 8015	EPA 3510	EPA 8015
PAH & Alkyl PAH	EPA 3580	EPA 8270	EPA 3510	EPA 8270
Alkyl Benzene	EPA 3580	EPA 8270A	EPA 3510	EPA 8270A
Antioxidant	EPA 3630A	EPA 8470	EPA 3510A	EPA 8270
Icing Inhibitor	ASTM D5006 mod	EPA 8270	EPA 3510 mod	EPA 8270
PIANO	ASTM D5134		-	-
Sulfur	ASTM D4294&D3120*		-	-
C, H, N	ASTM D5291		-	-

*: D3210 for determination of trace concentrations of sulfur/ D4294 for determination of sulfur at 0.015 to 5% mass of hydrocarbon

Pre: Pre-treatment of sample, mod: modified

REF: Bull. Geol Surv Japan Vol 30pp 241-245, 1979&Anal. Chem. Vol 47pp 1179-1185, 1975&ASTM Method D129-64

these materials, we can find out that they have different TPH patterns depending on their fuel type. Some of the differences were found in even TPH pattern kerosene and JP-8. But even though there were some differences in TPH pattern of C-9 part and C-15 part, the pattern could be identified only when the fuel type was singular, while it was impossible when they were mixed. However, we could not find differences among patterns of GS kerosene, SK kerosene and LG kerosene.

GC-FID pattern analysis of the samples collected was identified that 15 samples were contaminated by gasoline, 2 samples were contaminated by kerosene (or JP-8), 7 samples of BH-4, BH-5, BH-6, BH-7, BH-8, B01-868, 20K-217S were contaminated by mixture of gasoline and kerosene (or JP-8), and 2 samples of B01-877, B01-880 were contaminated by mixture of gasoline, kerosene (or JP-8) and diesel. However, GC-FID pattern analysis was impossible to distinguish between kerosene and JP-8.

Homogeneity of oils can be traced using the ratio between pristane and phytane of oil components. This is due to the fact that pristane and phytane, of branched saturate isoprenoids, are not decomposed easily by microorganisms, and their ratios remain the same environmentally for a long time. Seoul City obtained data of m/z 85 GC-MS (SIM) by extracting free products and groundwater samples which were collected twice.

SC measured the ratio of pristane/phytane of oil components and found that the ratio of LG-white kerosene was 3.10, that of SK-white kerosene was 3.58 and that of GS-kerosene was 3.76, all of which double the value of JP-8 (1.77). It was useful in distinguishing between similar two fuel types in the pattern of TPH. And, the pristane/phytane ratio of LG-boiler kerosene with significant differences between JP-8 and TPH pattern was 1.3, SK-boiler kerosene was 1.55 and diesel was 0.79. As for the analytical result of the first free product sample, the ratio of pristane/phytane in most of the sample identified as kerosene(or JP-8) in TPH pattern analysis was 1.67-1.86 and the ratio for the second sample was 1.71-1.78, very similar to the ratio of JP-8.

3.2 Alkyl benzene and alkyl PAH

SC carried out pattern analysis of alkyl benzene to identify contaminated fuel type of groundwater around Noksapyong subway station. The pattern of alkyl benzene was very useful in identifying fuel type in the environmental sample transformed by weathering. SC used SIM mode of GC-MS for the pattern analysis of alkyl benzene in samples and chose ions of C6-benzene (162), C7-benzene (176) and C8-benzene (190). An additional peak group was found behind the alkyl benzene pattern of kerosene in the alkyl benzene pattern of JP-8. In general, kerosene passes through a desulfurization process unlike JP-8 under the condition of heating and resolution. Because of that, it is assumed that there were partial removals or modifications in the tail of kerosene. Therefore the additional tag that appears in alkylbenzene pattern of JP-8 takes an important role in differentiating kerosene and JP-8. Alkyl benzene pattern was very effective in distinguishing between JP-8 and kerosene and was not greatly interfered by the presence of a large amount of other fuel type. Using alkyl benzene pattern, 30 samples of BH-1, BH-2, BH-3, BH-4, BH-5, BH-6, BH-7, BH-8, BH-16, BH-31, BH-32, B01-730, B01-788, B01-868, B01-869, B01-870, B01-874, B01-875, B01-880, RW02-103, RW02-106, RW02-107, RW02-108, 19K-890, 20K-187C, 20K-203C, 20K-217S, 20K-230C, 20K-230S, 20K-246S (Fig. 89) were identified as JP-8 rather than kerosene. Fig 2 showed a comparison of alkylbenzene patterns of JP-8 and kerosene.

Alkyl PAH pattern including peaks of n-C9-, n-C10-, n-C11-, n-C12-, n-C13-alkane was used to distinguish between kerosene and JP-8. The results of sample analysis showed that BH-5, BH-6, BH-7, B01-868, 19K-890 and RW02-106 were contaminated by JP-8.

3.3 Antioxidants and icing inhibitor

Detection of antioxidants in environmental sample can be the evidence that the kerosene found in groundwater around Noksapyong subway station is JP-8, since antioxidant of phenol type is used in JP-8 only as an oil additive domestically. Detection of JP-8 can be considered as a clue that the polluter is American Army since JP-8 is used only in American Army Base around Noksapyong subway station.

The antioxidants used in JP-8 domestically are 2, 4-dimethyl-6-tert-butylphenol (DMTBP). we obtained the result of measurement of GC-MS (SIM) by extracting - according to test methods - free product samples and groundwater samples which have been collected twice and

analyzed the antioxidants out of gasoline, white kerosene, boiler kerosene, JP-8 and diesel control standard sample from LG oil station and SK oil station, and a gas station (GS) in American Army Base and ground ASTs around Noksapyong subway station. According to the analytical result of the fuel control standard sample obtained from oil stations, 12.3 mg/L of DMTBP was measured in AST(JP-8) sample in American Army Base, while DMTBP was not detected in gasoline, white kerosene, boiler kerosene and diesel control standard samples from LG oil station and SK oil station.

The fact that high concentrations of 180-2,890ug/L of 2,4 -dimethyl-6-tert-butyl phenol were detected in the free product samples, BH-6, BH-7,19K-890, B01-874, B01-877 and B01-880. This is an unavoidable evidence to show that they were contaminated by JP-8. An antioxidant, 2,4-dimethyl- 6-tert-butyl phenol was detected from BH-5, BH-6, BH-7, 19K-890, B01-788, B01-874, B01-877 and B01-880 samples.

Of JP-8 additives for jet fuel, icing inhibitor is a representative additive. A frequently used icing inhibitor is DEGME (diethylene glycol monoethyl ether). As for JP-8 obtained from ASTs samples in American Army Base, DEGME was 1,951.8ppm. Icing inhibitors of free product samples and groundwater samples were analyzed, but any icing inhibitor was not detected.

3.4 Sulfur Content, PIANO

Analysis of sulfur content found in fuels can be used to identify kerosene and JP-8.

The difference between kerosene and JP-8 with different quality standards of sulfur content is in their production processes. Kerosene requires deep desulfurization through hydrorefining, while JP-8 uses Merox process eliminating only mercaptane with a bad smell to get rid of sulfur. The hydrorefining process of kerosene involves mixing hydrocarbon base oil and hydrogen, and then contacting the mix to a catalyst under high pressure and temperature to eliminate sulfur constituent, separated into H₂S, and nitrogen constituent, separated into NH₃, when olefins are transformed into saturated hydrocarbons. Therefore, kerosene has relatively more saturated hydrocarbons and hydrogen content and less nitrogen content than JP-8.

While sulfur content of kerosene produced by domestic 5 petroleum companies in 2002 was as low as 5~40 mg/L, sulfur content of JP-8 with below 3,000 mg/L of quality standard (KS, ASTM, MIL-DTL-83133X Quality Standard) showed actually 400~2,000 mg/L. JP-8 rich-sample(BH-5, BH-6, BH-7, B01-868, 19K-890) contain high concentration of sulfur. Sulfur content was observed from 195 up to 1416mg/L in 1st survey, and from 120 up to 13861416mg/L in 2st survey.

PIANO compounds mainly take an important role in determining the physical characteristics of gasoline constituent. However, since increasing boiling point makes complete analysis of components leading to lower identification ratio, those compounds are not so meaningful in kerosene (jet fuel) constituent and beyond.

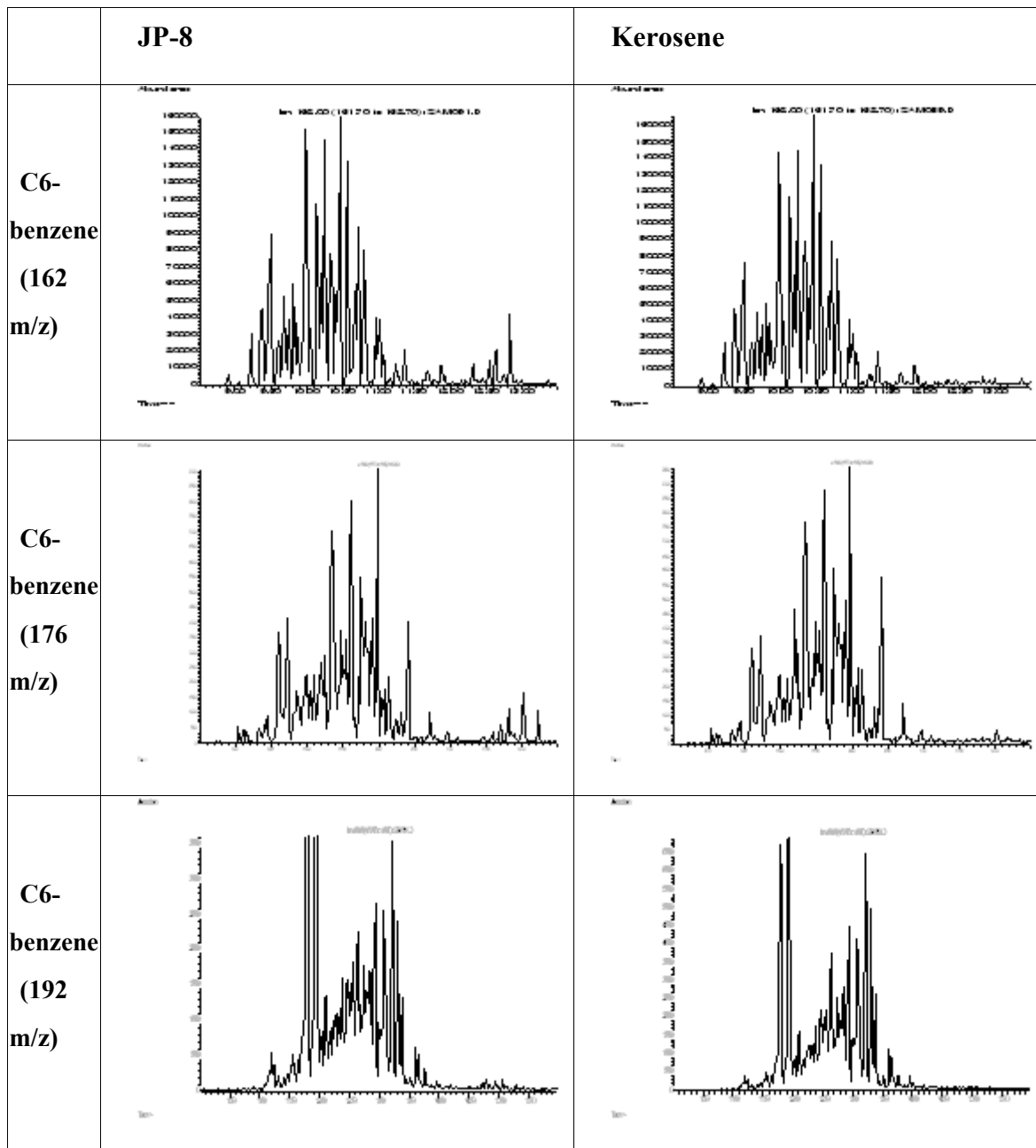


Figure 2. Comparison of alkylbenzene patterns of JP-8 and kerosene

4. CONCLUSION

According to the result of a variety of analytical methods to find the source of spilled fuel, i.e. the contaminant that caused fuel contamination of groundwater in tunnel of Noksapyong subway station in Seoul City, it has been found that the fuel type detected in the tunnel of Noksapyong subway station and the monitoring wells outside of Yongsan Garrison and the one

well inside of Yongsan Garrison are the same. The USFK did not recognize it before, but the exact fuel type was JP-8. Since JP-8 has been only by the USFK, we conclude that the source of fuel contamination in the groundwater wells around Noksapyong area and Subway tunnel is identified as the same source as the fuel discovered in the Yongsan Garrison.

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