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WATER SOLUBLE PHASE OF NUMBER 2 FUEL OIL: RESULTS OF A LABORATORY MIXING EXPERIMENT

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ABSTRACT

Ground water pollution from home heating oil (number 2 fuel oil) is widespread in New Jersey. To establish a baseline of water soluble components, a sample of home heating oil was mixed in water and the water phase extracted and analysed using US EPA Methods 624 + 15 (volatile organics) and 625 + 15 (base neutral and acid extractable compounds). Non-targeted compounds were tentatively identified using a mass spectra library search. Non-targeted volatile organics identified using Method 624 accounted for 79.5 percent of the compounds found; non-targeted base/neutrals accounted for 13 percent, priority pollutant volatile organics 4 percent and priority pollutant base/neutrals, 3.5 percent.

INTRODUCTION

Ground-water pollution from home heating oil is widespread in New Jersey (New Jersey Department of Environmental Protection, 1987). A common problem has been fuel oil odors in a water supply, but analysis of water samples from that same supply may not detect the presence of contamination. This may be due in part to components of the fuel oil that have odor thresholds below the current detection limits of laboratory analytical methods. Alternatively, inappropriate analytical methods may have been utilized on the water samples. The objective of this study was to identify the water soluble phase of home heating oil (no. 2 fuel oil) in order to establish a baseline of data for comparison to field results and to eliminate much of the confusion over which analytical methods to use. Based on the results of this mixing experiment along with analytical results from actual spill investigations, sampling and analytical methods for no. 2 fuel oil in water are recommended using standard US EPA Methods.

PROCEDURE

A sample of no. 2 home heating oil was collected in June 1987 from a below-ground residential heating oil tank in Morrisville, Pennsylvania. The fuel oil sample was mixed with carbon filtered water at a ratio of 1 part fuel oil to 5 parts water using a volatile organic vial and one liter glass containers equipped with teflon caps. The samples were agitated for 24 hours. The water phase was siphoned off into a separate container for analysis. The water phase was analyzed using the following methods:

1) Priority pollutant Base/Neutrals (BN) and acid extractable analysis using US EPA Method 625 (Federal Register, 1984).

2) Priority pollutant Volatile (purgeable) Organics (VOs) using US EPA Method 624 (Federal Register, 1984).

3) The base/neutral, acid extractable and volatile organic fractions were library searched through a computerized National Bureau of Standards (NBS) library of mass spectra to tentatively identify and quantify non-targeted compounds in each fraction.

RESULTS

A summary of analytical results is shown in tables 1 and 2. The chromatograms for Methods 624 and 625 are shown in figures 1 and 2, respectively. The results are summarized below:

1) Priority pollutants and non-targeted compounds were found in the VO analysis (EPA Method 624 + 15) and the BN analysis (EPA Method 625 + 15). The total VO (priority pollutant and non-targeted compounds) plus BN compounds (priority and non-targeted compounds) was 88,000 ppb.

2) No acid extractable compounds (priority or non-targeted compounds) were detected.

3) In the BN analysis (EPA Method 625), four priority pollutant BNs were identified at concentrations between 65 and 2,542 ppb. The total concentration of priority pollutant BN compounds was 3,078 ppb. In the non-targeted BN fraction, 15 compounds were tentatively identified with concentrations ranging from 375 to 1,380 ppb. The total concentration of non-targeted BN compounds was 11,405 PPB.

4) In the VO analysis (EPA Method 624 + 15) three priority pollutant compounds were found (benzene, toluene and ethylbenzene) with a total concentration of 3,693 ppb. In the non-targeted VO fraction, 19 compounds were tenatively identified ranging in concentration from 97 to 20,000 ppb. Total non-targeted VO concentration was 69,846 PPB. The predominant non-targeted VO compounds were alkylcyclohexanes and alkylbenzenes.

5) In the VO analysis, compounds began to elute 11 minutes into the run and were continuing to elute after 35 minutes (figure 1).

6) In the BN analysis, compounds began to elute 8 minutes into the run and continued to elute until 36 minutes into the run (figure 2).

7) The total concentration of VOs (targeted and non-targeted compounds) was 5 times greater than total BN (targeted plus non-targeted compounds) concentrations. VOs accounted for 84 percent of the total VO and BN compounds.

8) Total concentrations of non-targeted VOs were 19 times greater than the priority pollutant (targeted) VO compounds.

9) Total concentrations of non-targeted BN compounds were 3.7 times greater than the priority pollutant (targeted) BN compounds.

TABLE 1. MIXING EXPERIMENT RESULTS WATER SOLUBLE PHASE OF NUMBER 2 (HOME HEATING) OIL USING US EPA METHOD 624 + 15.

	Scan Number	Concentration (ppb)*
Priority pollutant volatile organics		
benzene		646
ethylbenzene		1360
toluene		1680
Additional compounds		
m-xylene		3760
o,p-xylene		3770
MTBE		117
methyl isobutyl ketone		97
Non-targeted volatile organics (tentatively identified compounds, concentrations estimated)		
cyclohexane-methyl	837	950
pentalene, octahydro,-cis-	924	250
cyclohexane,1,2-dimethyl,-cis-	1002	460
cyclohexane, ethyl	1079	2400
cyclohexane, trimethyl	1158	4800
cyclohexane,1-ethyl-4-methyl	1221	1900
benzene,(1-methylethyl)	1269	12000
cyclopropane,1-methyl-2-(3-methylpentyl)	1299	450
1-octene,3,3-dimethyl	1400	3100
benzene,propyl	1425	2500
benzene,(1-methylpropyl)	1461	2200
benzene,(1-methylethyl)	1547	20000
benzene,1-ethyl-3-methyl	1598	6200
benzene,methyl (1-methylethyl)	1667	4400
benzene,methyl (1-methylethyl)	1716	490

*Concentrations are rounded off to 3 significant figures

TABLE 2. MIXING EXPERIMENT RESULTS WATER SOLUBLE PHASE OF NUMBER 2 (HOME HEATING) OIL USING US EPA METHOD 625 + 15 (BASE NEUTRAL FRACTION).

	Scan Number	Concentration (ppb)*
Base/neutrals		
fluorene		175
napthalene		2540
phenanthrene		296
pyrene		65
Non-targeted base/neutrals (tentatively identified compounds, concentrations estimated)		
decane	380	375
undecane	508	590
undecane,3,6-dimethyl	642	590
octane,2,3,7-trimethyl	710	800
tridecane	741	1030
napthalene, 1-methyl	756	1230
1H-indene,1-ethylidene	774	720
pentacozane	841	1380
napthalene,1,2-dimethyl	883	540
hexadecane	897	350
pentadecane	933	1170
tridecane,7-propyl	1020	925
decane,6-ethyl-2-methyl	1100	680
dodecane,2,7,10-trimethyl	1100	510
dodecane,2-methyl-6-propyl	1180	510

*Concentrations are rounded off to three significant figures

LIMITATIONS OF THE STUDY

Limitations of the mixing experiment were as follows:

1) The mixing study represents a "worst case" scenario of ground water contamination from home heating oil.

2) Non-targeted compounds were tentatively identified by attempting to match the mass spectra of the sample to a NBS library of similar spectra. Only the first 15 non-targeted compounds in the VO and BN fractions were tentatively identified. Additional non-targeted compounds may be present in the water phase.

3) The analytical methods used were limited to standard US EPA methodologies. Compounds may be present in the water phase of the fuel that cannot be detected using EPA Methods 624 and 625.

4) The study did not account for chemical reactions and biodegradation processes that may generate secondary pollutants in ground water after a spill incident.

5) Only a single analysis was conducted.

CONCLUSIONS

This mixing experiment was conducted to establish a baseline of water soluble components of no. 2 fuel oil. Table 3 sets forth recommended sampling and analytical methods for number two fuel oil in ground water using standard US EPA methodologies that most environmental laboratories should be capable of running. Much more work is needed in the area of analytical methods for fuel oils. A low cost, reliable analytical method needs to be developed specifically for these fuels that will insure detection of the wide range of water soluble compounds that compose them. Ironically, with all of the US EPA methodologies available today, field experience in New Jersey has shown that one's nose may be one of the most cost effective, sensitive detectors of fuel oil components in water supplies. It must be stressed that the authors are not advocating the use of the nose for detecting all ground water pollution, but in the case of fuel oils, given the current confusion over a suitable analytical method, odor should certainly be used in conjunction with laboratory services when checking for the presence of no. 2 fuel oil in water supplies.

TABLE 3. RECOMMENDED PROCEDURES AND ANALYTICAL METHODS FOR DETECTING NUMBER TWO FUEL OIL IN GROUND WATER

1) In any ground-water pollution case involving gasoline, fuel oils, kerosene, or diesel fuel, insure that at least three feet of well screen in the monitoring well extends above the water table in order to detect floating product.

2) All monitoring wells should be periodically checked for free product, sheens, and toxic/combustible gases in the headspace of the well.

3) Fuel oils have very low odor thresholds. Water supplies should therefore be checked for the presence of fuel oil odors. Ideally, a sample of hot water should be first agitated in a jar and then cheked for the presence of odors.

4) The presence of fuel oil odors, sheens, or free product in a water supply should be interpreted as evidence of ground water pollution. The water quality standard for odor, taste and petroleum hydrocarbons in ground water in New Jersey is NONE NOTICEABLE.

5) Water samples should be obtained within two feet of the static water level in the monitoring well.

6) Water from the "worst case" monitoring well as defined by the presence of odors, sheens, free product should be analyzed using:

   A) US EPA Method 624 plus the identification and quantification of 15 non-targeted compounds. The run should be continued for at least 40 minutes to insure elution and detection of fuel oil components.

   B) US EPA Method 625 (base/neutrals only) plus the identification and quantification of 15 non-targeted compounds.

   C) US EPA Method 418.1 (petroleum hydrocarbons). The sample must be collected at the water surface in the well.

7) All other monitoring wells should be sampled and analyzed using EPA Method 624 as listed in item 6A, above. At the discretion of NJDEP, monitoring wells that show visible evidence of contamination (sheens or free product) may not have to be sampled.

9) Analyses of water from supply wells for fuel oil components should be done using methodologies A, B, and C listed above. Supply wells should also be opened and checked for accumulations of free product or sheens at the water surface in the well.

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REFERENCES

Federal Register, 1984, 40 CFR Part 136, vol. 49, no. 209, pp. 141-152 and 153-174.

New Jersey Department of Environmental Protection, 1987, New Jersey Ground Water Pollution Index, New Jersey Geological Survey, Trenton

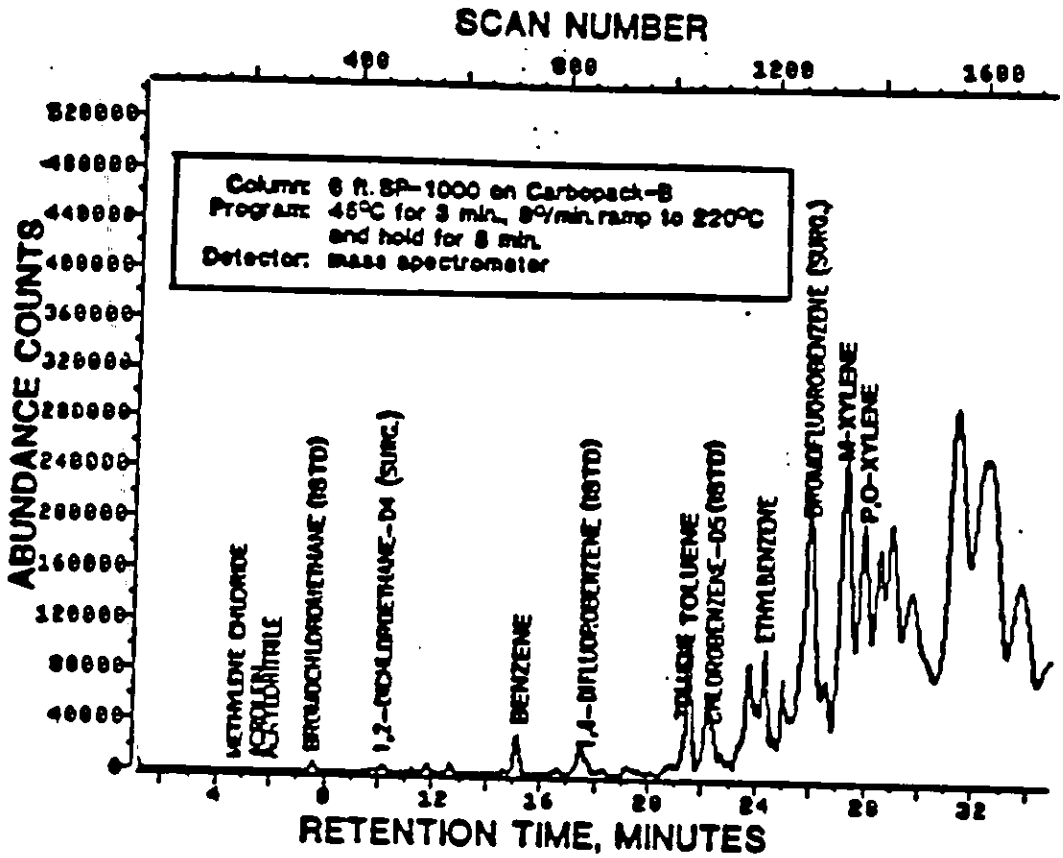

Figure 1. Total ion chromatogram of volatile organics for water soluble phase of No. 2 fuel oil (home heating oil) using EPA Method 624.

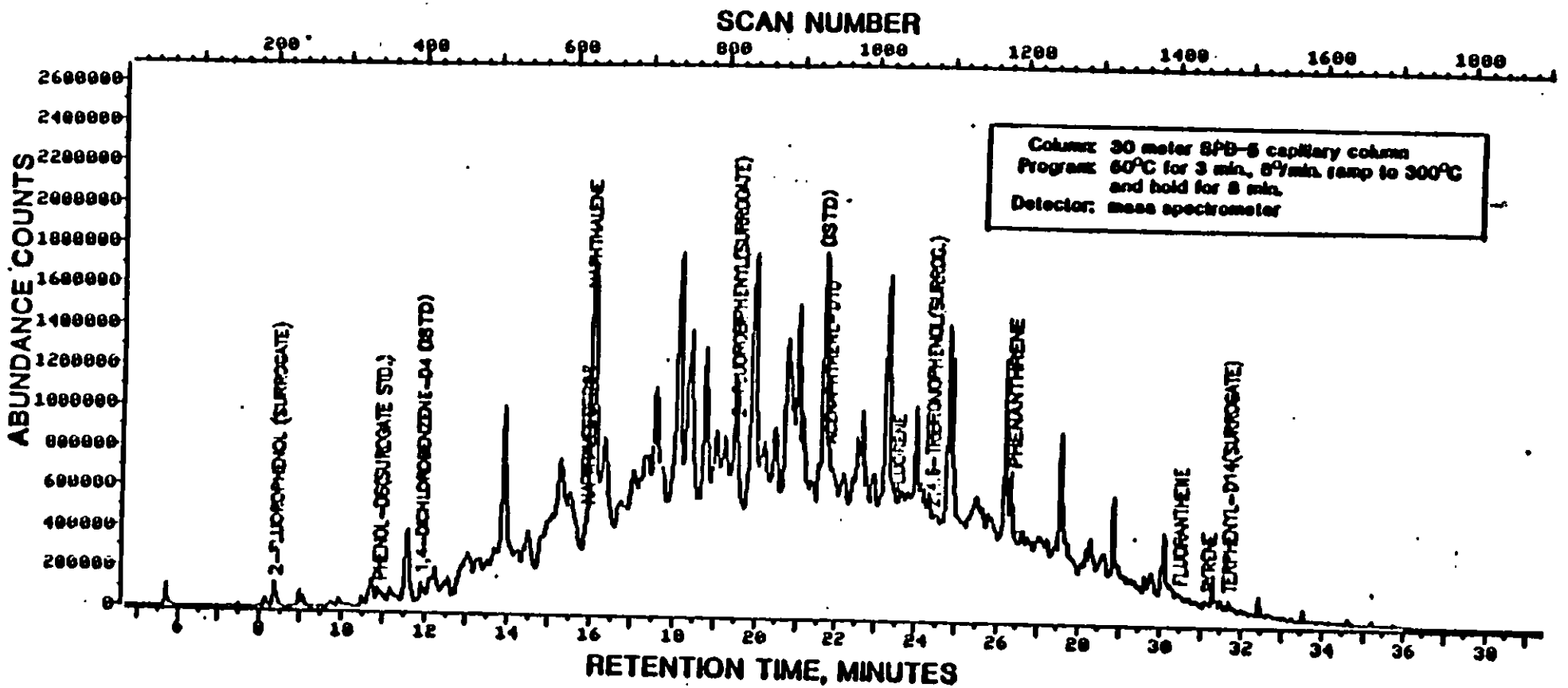

Figure 2. Total ion chromatogram of base/neutral fraction for water soluble phase of No. 2 fuel oil (home heating oil) using EPA Method 625.

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