NEW JERSEY GEOLOGICAL SURVEY
TECHNICAL MEMORANDUM 87-5

Water Soluble Phase of Gasoline:
Results of a Laboratory Mixing Experiment

Department of Environmental Protection
Division of Water Resources

1987

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WATER SOLUBLE PHASE OF GASOLINE: RESULTS OF A LABORATORY MIXING EXPERIMENT

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Presented at the National Meeting
American Public Health Association
New Orleans
October 1987

New Jersey Department of Environmental Protection
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ABSTRACT

Ground-water pollution from gasoline is widespread in New Jersey. Mixing experiments using gasoline and water were conducted using regular leaded (89 octane), regular unleaded (86 octane) and high octane unleaded (93.5 octane) gasoline to identify the water soluble components of the three fuels. After mixing, the water phase was extracted and analysed using US EPA Method 624 plus the identification of 15 non-targeted compounds. Selected additives and blending agents were also searched for. Four out of the 31 priority pollutant compounds listed on Method 624 were identified along with other targeted and non-targeted compounds. The results of the experiment help to establish a baseline of water soluble compounds found in gasoline for comparison to field situations, determine the relative abundance of these compounds in the water soluble phase and determine compositional differences between product grades. Appropriate analytical parameters are recommended for use in the field.

INTRODUCTION

Ground water pollution from gasoline is widespread in New Jersey (New Jersey Department of Environmental Protection, 1987). The problem of Leaking Underground Storage Tanks and piping (LUST) has been recognized as a national problem by US EPA. Subtitle I of the Resource Conservation and Recovery Act (RCRA) requires development of LUST regulations. Since gasoline is a complex mixture of hundreds of petrochemicals, selection of an appropriate analytical method for gasoline in ground water requires careful consideration.

From a regulatory/ground water perspective, there are a number of questions that should be considered. Among them are: what are the most water soluble components of the fuel? What are the most toxic components? Which components will arrive first at a downgradient point due to differing retardation factors? Is there a set of components that could be used as a reliable, cost-effective indicator of gasoline contamination in ground water? Will some components be degraded in the subsurface and transformed to more toxic or more soluble compounds? Are there any gasoline components with specific gravities greater than that of water?

The most common compounds used to test for gasoline in ground water have been benzene, toluene, and xylenes (BTX) and in some cases petroleum hydrocarbons (EPA Method 418.1). Method 418.1 is not recommended as an indicator of gasoline contamination due to the relatively high detection limits (0.5 to 1.0 ppm) and the expected loss of 50 percent of the gasoline that will occur during the extraction process.

The objective of this study was to obtain a baseline of water soluble gasoline components using standard US EPA analytical protocols plus a search for non-priority pollutants using a mass spectrometer library search. In addition, a limited list of additives and blending agents found in the field and in the literature were included in the analysis.

It was anticipated that the results of the mixing experiment would provide baseline data on water soluble gasoline components for use in comparison to compounds detected in the field. Such a baseline would allow differentiation between compounds that formed in the subsurface due to chemical reactions and to separate out pollutants from sources unrelated to gasoline. In addition, the baseline data could be used to compare relative concentrations of gasoline components in a new spill as opposed to concentrations that might be encountered from an older spill.

PROCEDURE

In September 1986 three grades of gasoline were collected from a gasoline retail outlet in New Jersey that received product from a major oil company. The grades collected were regular leaded, regular unleaded and a high octane unleaded. The samples were collected in glass stoppered vials and delivered to a NJDEP certified laboratory within one hour of collection. The gasoline samples were mixed for 24 hours with carbon filtered water at a ratio of 1 part gasoline to 1 part water in 40 ml glass vials with teflon caps. The water phase was extracted and analyzed using EPA Method 624, volatile organics (Federal Register, 1984). Duplicate analytical runs were performed on each of the three gasoline samples. The volatile organic scan results were library searched through a computerized National Bureau of Standards (NBS) library of mass spectra to tenatively identify non-targeted compounds.

RESULTS AND DISCUSSION

Of the 31 priority volatile organics listed in EPA Method 624, four were detected in the water soluble phase of the gasoline (table 1). In addition, two of the three additives and blending agents searched for were detected. Three other targeted compounds and five non-targeted compounds were tenatively identified and quantified in duplicate runs using the mass spectra library searches. The chromatograms of the water soluble phase of three grades of gasoline are shown in figures 1, 2, and 3. Note that only compounds that were tentatively identified in <u>both runs</u> are reported. Some observations are as follows:

1) Concentrations of other-targeted compounds and additives were twice as high as concentrations of priority pollutant volatile organics in the regular leaded grade and 10 times higher in the super unleaded grade.

2) Regular leaded and regular unleaded products had similar concentrations of water soluble components. Both leaded and unleaded products were found to contain the additives methyl-tertiary butyl ether (MTBE) and tertiary butyl

TABLE I: MIXING EXPERIMENT RESULTS, WATER SOLUBLE PHASE OF THREE GRADES OF GASOLINE USING US EPA METHOD 624 + 15.

	CONCENTRATION (ppb)*		
	REGULAR LEADED	REGULAR UNLEADED	SUPER UNLEADED
COMPOUND			
Priority Pollutants Volatile Organics			
benzene	30,500	28,100	67,000
toluene	31,400	31,100	107,400
ethylbenzene	4,040	2,420	7,400
1,2-dichloroethane	1,330	ND	ND
Ohter-targeted compounds and selected additives			
methyl-t-butyl ether (MTBE)	43,700	35,100	966,000
tertiary butyl alcohol(TBA)	22,300	15,900	933,000
di-isopropyl ether (DIPE)	ND	ND	ND
m-xylene	13,900	10,900	11,500
o,p-xylene	6,050	4,840	5,660
1,2-dibromoethane (EDB)	576	ND	ND
Tentatively Identified Compounds (Concentrations Estimated)			
2-butene	5,870	4,740	8,790
2-methyl butane	9,930	*	ND
2-pentene	22,500	*	ND
cyclopentene	5,190	ND	ND
2-butoxy ethanol	ND	ND	16,800
1,2,3 trimethylbenzene	*	*	*
1-ethyl-2-methyl benzene	ND	*	ND
1-ethyl-3-methyl benzene	*	ND	*

* - Detected in one run only
ND - non-detectable
Concentrations are rounded off to 3 significant figures.

alcohol (TBA).

3) The regular leaded product contained the lead scavengers 1,2-dichloroethane and 1,2-dibromoethane (EDB).

4) The high octane unleaded was enriched in benzene, toluene, ethylbenzene, MTBE and TBA. Xylene concentrations were similar to the regular leaded and regular unleaded grades.

5) Concentrations of butene in all three grades were close to the concentrations of ethylbenzene and o,p-xylenes in each of the grades.

6) The water soluble phase of the high octane unleaded product contained 2-butoxy ethanol (ethylene glycol monobutyl ether), tentatively identified in both runs. This compound did not occur in the regular leaded or regular unleaded grades.

7) High concentrations of acrolein were reported in the water soluble phase in all three grades. This compound has also been reported in water samples from spill sites in New Jersey contaminated by gasoline. The authors believe additional investigation using EPA Method 603 is required before the presence of acrolein can be confirmed.

8) o,m,p-dichlorobenzenes were also searched for in the water soluble phase of all three grades but were not detected. Dichlorobenzenes have been reported in ground water samples contaminated by gasoline.

LIMITATIONS OF THE STUDY

There were several limitations to this experiment as follows:

1) Product from only one company was collected and analyzed.

2) Additives and blending agents will vary over time as will the source and characteristics of the crude oil. The use of some additives and blending agents may have been discontinued.

3) The analytical methods used were limited to standard US EPA methodology along with a limited search for additives and blending agents commonly found during spill investigations. Other water soluble components may be present that were not detected by EPA Method 624 + 15. Because of dilution requirements, some compounds that were present below 500 ppb may not have been reported.

4) This study represents a "worst case" situation of free gasoline in contact with the water table. Soil attentuation was not considered.

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

CONCLUSIONS

Based upon results of this mixing experiment along with field data collected from years of ground-water investigations in New Jersey, standard analytical procedures are recommended (table 2) for use on ground water samples when gasoline contamination is suspected. These tests are standard US EPA methodologies that most environmental laboratories should be capable of running. Note in table 1 that dichlorobenzenes and methanol are listed as additional compounds to search for. Methanol was not searched for in this experiment, but is found in some ground water samples contaminated by gasoline.

ACKNOWLEDGEMENTS

The authors would like to thank William Sherding, Laboratory Supervisor and Vincent J. Pugliese, Environmental Laboratory Manager, Accutest Laboratories, North Brunswick, NJ for analytical services and technical support.

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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

TABLE 2: RECOMMENDED PROCEDURES AND ANALYTICAL METHODS FOR DETECTING GASOLINE IN GROUND WATER.

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

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

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

4) Ground water from the "worst case" monitoring well, as determined by the presence of free product, sheens, odors and/or field instruments (PID or FID detectors), should be analyzed using US EPA Method 624 plus the identification and quantification of 15 non-targeted compounds. In addition, the following compounds should be searched for:

   o,m,p-xylenes
   o,m,p-dichlorobenzenes
   methyl-t-butyl ether (MTBE)
   diisopropyl ether (DIPE)
   methanol
   tertiary butyl alcohol (TBA)
   1,2,-dibromoethane (EDB)

5) All other monitoring wells should be sampled for benzene, toluene, ethylbenzene, o,m,p-xylenes (BTEX), MTBE and TBA. Analytical methods can be modified pending review of water quality results in the "worst case" well(s). At the discretion of NJDEP, monitoring wells that show visible evidence of contamination (sheens or free product) may not have to be sampled.

6) EPA Method 418.1 should not be used for detection of gasoline components in water.

7) Consideration should also be given to the presence of other compounds in the ground water that result from biodegradation or other chemical alteration of the fuel. For example, Barker and others (1987) report the presence of phenolic compounds as a result of degradation of benzene, toluene and xylenes in laboratory experiments.

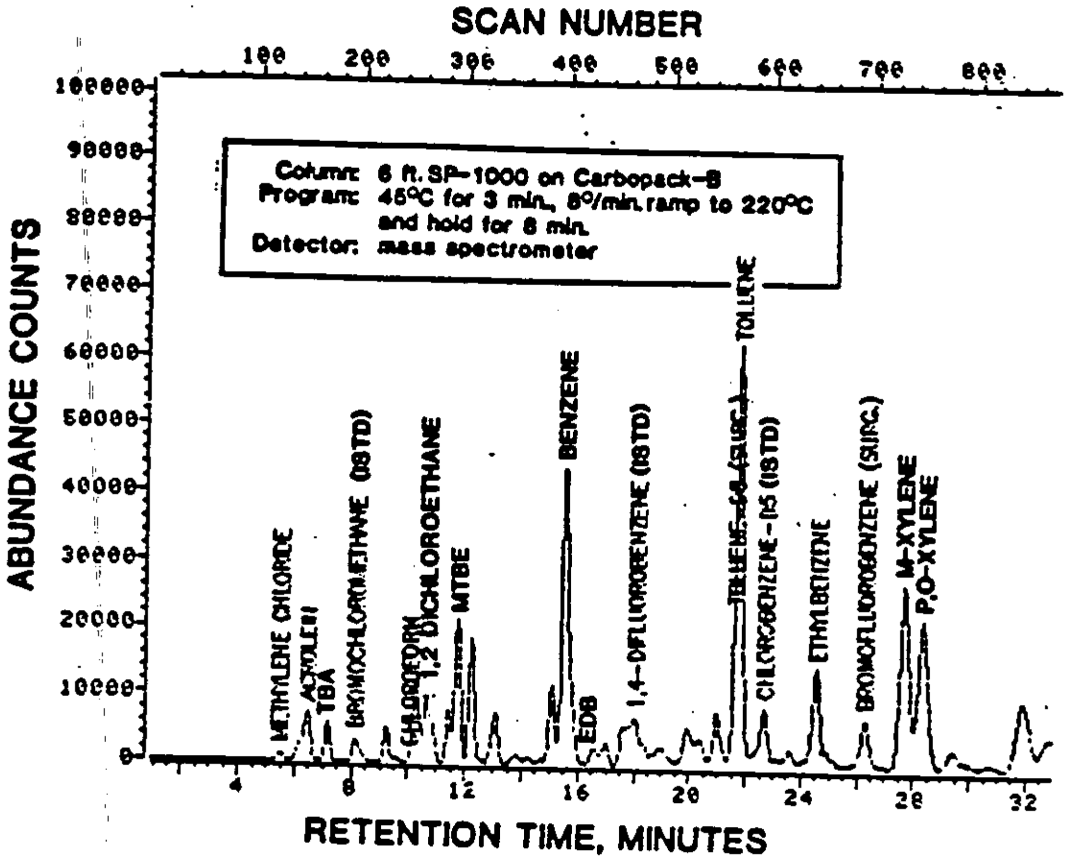

Figure 1. Total Ion chromatogram of volatile organics for water soluble phase of regular leaded gasoline using EPA Method 624.

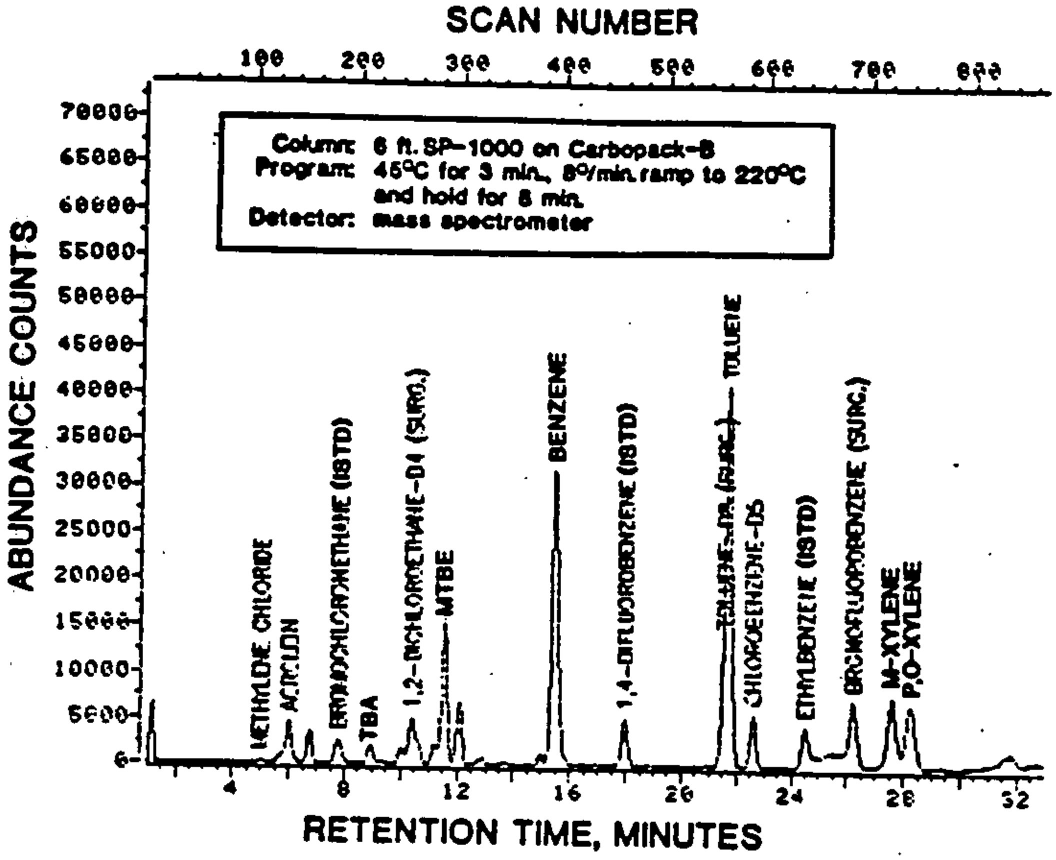

Figure 2. Total ion chromatogram of volatile organics for water soluble phase of regular unleaded gasoline using EPA Method 624.

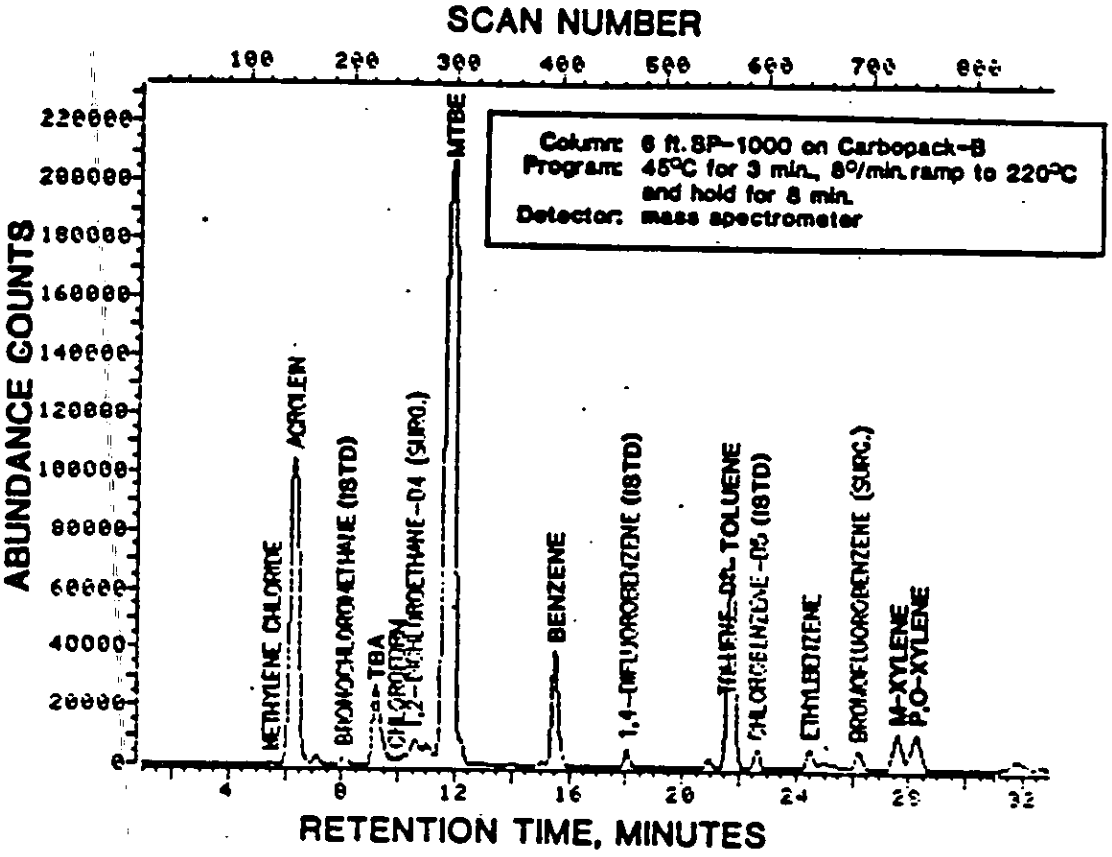

Figure 3. Total ion chromatogram of volatile organics for water soluble phase of high-octane unleaded gasoline using EPA Method 624.

WATER SOLUBLE PHASE OF GASOLINE: RESULTS OF A LABORATORY MIXING EXPERIMENT (N.J. Geological Survey Technical Memorandum 87-5)