5-31-1992

Measurement of VOCs pollution from recycling petroleum contaminated soils in hot mix asphalt concrete

Yaoqing Chen
New Jersey Institute of Technology

Recommended Citation

Chen, Yaoqing, "Measurement of VOCs pollution from recycling petroleum contaminated soils in hot mix asphalt concrete" (1992). *Theses*. 2238.
https://digitalcommons.njit.edu/theses/2238

ABSTRACT

Measurement of VOCs Pollution From Recycling Petroleum Contaminated Soils in Hot Mix Asphalt Concrete

by
Yaoqing Chen

The petroleum contaminated soils (PCSs) due to leaking underground storagetanks are required to be removed and isolated in a designated area for proper treatment. Recently, a technique of recycle has been developed to incorporate PCSs into hot mixing asphalt (HMA) as a partial substitute for stone aggregate; the mixture then was used for road paving.

This study focuses on the estimation of the emission of volatile organic compounds from the process of mixing asphalt with PCSs and the contamination of ground water by paving the asphalt mixture made with PCSs. Eleven volatile organic compounds and total non-methane organic compounds emitted from the asphalt mixing process were measured by solid adsorbent sampling and thermal desorption, followed by gas chromatographic analysis. An uniform leachability test was designed to simulate the VOCs release to ground water as asphalt mixtures with PCSs were paved on roads.

The results showed that the mixing process of PCSs with asphalt can increase VOCs emission, but there was no severe air pollution problem. There was insignificant VOCs leaching from this mixture to ground water. Therefore, from the environmental aspect, this technique is a feasible method to remediate and reuse PCSs.

MEASUREMENT OF VOCs POLLUTION FROM RECYCLING PETROLEUM CONTAMINATED SOILS IN HOT MIX ASPHALT CONCRETE

by
Yaoqing Chen

A Thesis
Submitted to the Faculty of
New Jersey Institute of Technology
in Partial Fulfillment of the Requirements for the Degree of
Master of Environmental Science
Department of Chemical Engineering, Chemistry,
and Environmental Science
May 1992

APPROVAL PAGE

Measurement of VOCs Emission from Recycling Petroleum Contaminated Soils in Hot Mix Asphalt Concrete

by

Yaoqing Chen

Dr. Namunu J. Meegoda, Thesis Advisor.
Associate Professor of Civil & Environmental
Engineering, NJIT

Dr Barbara B. Kebbekus, Committee Member
Professor of Chemical Engineering,
Chemistry & Environmental Science,
NJIT

Dr Somenath Mitra, Committee Member
Assistant Professor
of Chemical Engineering, Chemistry &
Environmental Science, NJIT

BIOGRAPHICAL SKETCH

Author: Yaoqing Chen

Degree: Master of Science, 1992

Date: May, 1992

Date of Birth:

Place of birth:

Undergraduate and Graduate Education:

- Master of Science in Environmental Science, New Jersey Institute of Technology, Newark, NJ, 1992
- Bachelor of Science in Medicine,Fujian College of Medicine, Fujian, P.R. China, 1982

Major: Environmental Science

Presentations and Publications:

Chen, Yaoqing., and Namunu J. Meegoda. " A Rapid yet Inexpensive Method to Monitor Air Quality in Asphalt Concrete Plants" Asphalt Research 5 (1992):54

ACKNOWLEDGMENT

The author would like to express his most sincere appreciation to his advisor Dr. Namunu J. Meegoda for his guidance, encouragement and support throughout the work. He would also like to thank his other advisory committee members Dr. Barbara B. Kebbekus and Dr. Somenath Mitra for their helpful guidance, their valuable time and efforts.

In addition, he would like to extend his most sincere gratitude to Mr. Clint Brockway for his great help, friendship and help discussions.

TABLE OF CONTENTS

Page

LIST OF TABLES

Table **Page**

LIST OF FIGURES

Chapter 1
INTRODUCTION

1.1 BACKGROUND

During 1950s and 1960s, the construction of many gasoline stations, chemical manufacturing and processing facilities led to the installation of millions of underground storage tanks(USTs). Several million USTs in the United States contain petroleum. Tens of thousands of these USTs, including their piping, are currently leaking (1). US EPA estimates that the number of leaking USTs with petroleum hydrocarbons range from 100,000 to 400,000. Many more are expected to leak in the future.

Leaking USTs can cause fires or explosions that threat human on safety. In addition, leaking USTs can contaminate nearby ground water. The degree of contamination and the effects on human health and the environment depend on the amount of fuel released, the chemical and physical properties of the material, the hydrogeologic conditions of the site and resulting fluid migration patterns, and levels of exposure to potential receptors. Most states vigorously encourage the removal of all tanks after 25 years of service. It is estimated that on average each removal of a leaking tank will generate 30 to 50 cubic yards of contaminated soil. Since groundwater is the major source of drinking water, Federal legislation seeks to safeguard our nation's ground water resources. Congress responded to the problem of leaking USTs by adding Subtitle I to the Resource Conservation and Recovery Act in 1984. The federal and state's statues require such leaking USTs be removed to prevent further contamination.

Gasoline, diesel, and fuel oil are the most common petroleum hydrocarbons used and consequently are the ones that most likely will leak from underground storage tanks. Each of these products is a complex mixture of organic compounds with specific physical and chemical properties and behavior, when in contact with subsurface soil and waters.

The major chemical components of petroleum hydrocarbons are alkanes, cycloalkanes, and aromatics.

The physical and chemical characteristics of each fuel material depend on the type (gasoline, diesel, and fuel oil) and the source from which it is extracted. Gasoline is the most volatile of the three mixtures of petroleum hydrocarbons. The major chemical components include branched chain paraffins, cycloparaffins and aromatics. Diesel is No. 2 fuel oil. It is primarily cpmposed of unbranched paraffins with a flash point between 43° and 88°C(110° and 109°F). Fuel oils are chemical mixtures having flash points greater than 37°C(100°F). Composition of fuel oil vary much more than that of gasoline and diesel.

Leaking underground storage tanks present an enormous hazard that has received scant attention until recently. Under EPA rules, owners of petroleum USTs are responsible for corrective action. They must clean up any petroleum leaks and correct any resulting environmental damages.

1.2 REMEDIATION TECHNIQUES FOR PCSs

The contaminated soils resulting from leaking USTs are required to be treated in-situ, or removed in an isolated area for proper treatment or disposal. There are many in-situ/on-site/off-site treatment and disposal options available for deconta-mination of PCSs (2). Selection of the most cost-effective option(s) depends on engineering factors such as soil characteristics, site geology, lateral extent of con- tamination, depth of contamination, topography, location, climate, surface and ground water conditions, type and amount of chemicals. The currently available technologies for soil or groundwater impacted by leaking USTs may be categorized as : 1. Preventing migration of contaminants. 2. Recovering PCSs. 3. Removing dissolved contaminants in the groundwater. These treatment technologies are explored based on their commercial availability, regulatory requirements, cost, implimen tabi lity, timing, space, liability and reuse potential. Further factors such as on-site applications, short-term and long-term effectiveness, community acceptance, in-situ applications and environmental concerns make certain technologies highly desirable.

An effective treatment for released petroleum hydrocarbons requires understanding site conditions and defining appropriate remediation goals. These vary from site to site and can range from immediate action to removal of all petroleum product from site to site and can renge from immediate action to removal of all petroleum products from the subsurface. Selecting the technology that best meets these goals involves identifying potential impacts to the surrounding environment, recognizing the regulatory restrictions that may govern clean up criteria, and evaluating the likely effectiveness of alternative technologies.

1.2.1 Prevention of contaminant migration:

These methods involve the separation of contaminated area from the environment with containment devices or the addition of an additive to stabilize the contaminants, such as trench excavation, pumping wells, solidification, soil cooling and freezing, vitrification.

(1). Trench excavation:

A very simple way to prevent migration of contaminants is to dig a trench to intercept the downgradient of the plume. When trenches are used to contain and remove free product, removal efforts must be continuous. Otherwise the product will migrate to the ends of the trench and possibly pass the impermeable baffle (3).

(2). Pumping well:

Pumping well is an effective and commonly used method for containing contaminants in the saturated zone. The basic concept of this method is to artificially lower the water table at the site, drawing local groundwater and contaminants to the well. The two most important considerations in this method are well location and pumping rate (3).

(3). Solidification/stabilization:

Solidification/stabilization involves the addition of an additive to excavated soil to encapsulate compounds of contaminants. This method requires that all wastes are thoroughly mixed in a homogenous form to assure chemical characteristic integrity throughout the treated waste. Solidification/stabilization has been used primarily with inorganic toxic wastes to immobilize the contaminants, but some studies showed petroleum wastes, especially high molecular weight hydrocarbon, can be successful solidification. Many of these additives are not effective in stabilizing organic contaminants, however, recent studies indicate that modified clays can be used to immobilize organic contaminants (4). A recent report has shown that the total petroleum hydrocarbon can be successfully stabilized (5). Volatile organic compounds were difficult to be immobilized in most case studies.

(4). Vitrification:

In situ vetrification is a thermal process by which contaminated soils are converted into chemically inert and stable glass and crystalline materials. Field application requires the insertion of large electrodes into contaminated soil containing significant levels of silicate material and applying electrical power to generate heat (up to 3600 °C). Any gases and vapors produced can be collected by a hood above the treated area to draw them for further treatment. After the process is terminated and the ground has been cooled, the fused waste material will disperse into a chemical inert and stable crystalline form that has very low leachability rates and almost the same chemical stability as granite. This process eliminates excavation, processing, and reburial of the hazardous compounds, so minimizes exposure of contaminants (6).

(5). Soil Cooling and Ground Freezing:

Soil cooling is a technique for decreasing soil temperature so as to reduce the vapor pressure of volatile constituents and their volatile rates. This technique is a temporary remediation method, as the contaminants are bound only by the frozen water in the soil. One way to lower soil temperature is to apply cooling agents to the soil surface. Because of the effectiveness of solid carbon dioxide and the minimal risks it poses for response personnel during its application, it was the cooling agent of choice.

Ground freezing is another means of immobilizing contaminants. Ground freezing involves injecting a cooling agent into pipes located within the soil matrix, which cools the soil to far below the freezing point of water. This technique is apparently most suitable for immobilizing volatile organic compounds at hazardous waste sites. The use of cooling and freezing agents would not be reliable for large areas or for long periods of time (7).

1.2.2 Recovery of PCSs:

Various types of removal methods can be used for remediation of PCSs, such as incineration, vacuum extraction, soil flushing, soil washing, oxidation treatment, and radio frequency heating.

(1). Incineration:

This method is a process that utilizes high or lower temperature to destroy or volatilize hydrocarbons. Incinerators that can potentially be used for the treatment of PCSs included: (1)fluidized bed; (2)rotary kiln; (3)pyrolysis; (4)infrared; and (5)multiple hearth. In high temperature, the destruction and removal efficiency achieved for wastes incinerated properly operated thermal process often exceeds 99.9 percent. The weight and volume of combustible waste may be reduced by more than 90 percent through incineration. Air pollution control devices may be needed to effectively reduce the potential particulate emission and volatile organic compounds. The low-temperature thermal treatment is designed to heat and agitate the soil that volatile organic compounds are released from the soil matrix. The volatile organic compounds are then collected in a solvent recovery system or combusted in afterburner. The low-temperature thermal treatment can decrease energy requirements and operation cost (8).

(2). Vacuum extraction:

This technique involves extraction of air from unsaturated soil. Clean air is injected or passively flows into the unsaturated zone where volatile chemicals partition from soil water into soil air, with relative partitioning based on the air/water coefficient or Henry's Law constant.

Typically, the system consists of vacuum extraction well, air inlet well, and vapor monitoring wells distributed across a contaminated site, and a blower to control air flow. As vast volumes of soil vapor are removed by the vacuum process, fresh air naturally recharges the vadose zone from the surface. Fresh air moves through the contaminated zone as VOCs are partitioned from the soil matrix to the vapor phase and move to the extraction wells. Since VOCs vaporize readily, the vacuum extraction process continually drives the contaminants from the soil matrix to the vapor state. Progress of the vacuum extraction system can be monitored by the concentration of the extracted vapors. This technique effectively removes volatile and semi-volatile compounds from soil. A promising aspect of vacuum extraction is potential application for the enhancement of biodegradation of volatile and semi-volatile chemicals in soils (9).

(3). Soil Flushing:

Removal of organic contaminants from PCSs may be accomplished using soil flushing, with recovery and treatment of the elutriate. Flushing solutions generally include water, acidic and basic solutions, surfactants, and solvents. The function of solutions is to partition a contaminant into the liquid phase through volume of added liquid or through decreasing the distribution coefficient between the soil and the flushing phase. After flushing, the leachate is injected through the soil zone to a collection system, then pumped to the surface for removal of contaminant. Because petroleum oils are hydrophobic, surfactants and solvents are likely to be more effective than water. This method is less effective in unfavorable soil characteristics, such as soil with high silt and clay content, high organic matter content. The flushing solution must be easy to recover with good treatability and low toxicity (10).

(4). Oxidation treatment:

Ozone, the most powerful technically applied oxidizing agent, is able to destroy hydrocarbons when a gas stream enriched with ozone is passed through the contaminated soil.

There are two mechanisms in ozone treatment: (1)direct reaction. (2)decomposition of the ozone to intermediates(e.g.,radicals), which in turn react directly or indirectly with hydrocarbon. The pollutants may be reduced by up to 98 % of the original concentration but the efficiency depends on several parameters,e.g., the nature of pollutants, the condition of soil, especially its permeability to gas, and the presence of accompanying substances (humic material). Ozone treatment may be carried out in-situ as well as on-site and off-site (11).

UV/oxidation as a water treatment technique is rapidly expanding. It utilizes ultraviolet light catalyzed ozone plus hydrogen peroxide to oxidize organic compounds and offers a method of destroying on site many of contaminants found today in groundwater (12).

(5). Radio Frequency Heating:

Radio frequency heating is a technique for rapid and uniform in situ heating of large volumes of soil. This technique heats the soil to the point where volatile and semivolatile contaminants are vaporized into the soil matrix. Vented electrodes are then used to recover the gases formed in the soil matrix during the heating process. The concentrated extracted gas stream that is recovered can be incinerated or subjected to other treatment methods. The mechanism of heat generation is similar to that of a microwave oven. The heating process does not rely on the thermal conductivity of the soil. The exact operational frequency is obtained from an evaluation of the area extent of contamination and the dielectric properties of the soil matrix (13) .

1.2.3 Removal of dissolved contaminants from groundwater:

(1). Biological treatment

Bioremediation relies on naturally occurring or genetically altered microorganisms to transform contaminants to less hazardous compounds. Bioremediation of contaminants is enhanced by the addition of oxygen and nutrients. Bacteria capable of biodegrading petroleum hydrocarbons are commonly found in subsurface soils and some natural breakdown of hydrocarbons released to the subsurface is likely to occur at all sites. However, without the addition of nutrients and oxygen, bioremediation usually occurs very slowly. This method is not as widely used as air stripping or carbon adsorption, but under the right conditions, bioremediation can be very cost-effective and its use is likely to grow in the future. Bioremediation of hydrocarbon can occur aerobically or aerobically, but it is widely accepted that aerobic processes are far more effective in biodegrading petroleum hydrocarbons than anaerobic processes. In-situ and on-site bioremediation are commercially available.

In-situ bioremediation can lessen the risk of exposure incurred when contaminants are brought to the surface. In this process, a sumersible pump transports groundwater from a recovery well to a mixing tank. Nutrients such as nitrogen, phosphorus and trace metals are added to the water in the mixing tank. Prior to reintroduction of the conditioned groundwater to the soil, hydrogen peroxide is added to the mixing tank. This conditioned water is then pumped to a injection well which reintroduces the conditioned water the soil. The conditioned water from injection well through the contaminated soil area then flows back to the recovery well. Enhancement of bioremediation may involve: (1)control soil factors such as moisture, pH, nutrients, and temperature to optimize microbial activity; (2)addition of colloidal gas aphrons(microscopic bubbles of gas) to increase the concentration of terminal electron acceptor (oxygen) in the soil and thereby enhance aerobic biodegradation (14).

(2). Air stripping:

Air stripping is one of the most common methods used to remove hydrocarbons from groundwater in the United States. Air stripping removes contaminants from groundwater through a controlled disequilibrium designed to promote the transfer of contaminants from the dissolved phase to the vapor phase. This is accomplished for all air stripping methods in two basic ways: (1)the surface area of the contaminated groundwater is increased, thus increasing the opportunity for volatilization; (2)a non-equilibrium conditon created between the liquid and gaseous phases by replenishing the supply of clean air to the system through either natural or induced means.

An innovative in-situ steam/hot air stripping technique was used to remove volatile compounds and semivolatile compounds from contaminated soil. In-situ steam/hot air stripping technology can treat saturated or unsaturated soil down to a depth of 30 feet as well as ground water. The unit consists of three connected components: (1)a steam generator; (2)a box, called a shroud, with a drill; and (3)a gas processing unit. At the site, the drill moved down through the shroud into the soil column where it injected steam and hot air from the steam generator into the soil column. The steam and hot air caused the contaminants to volatilize and be forced up through the column into the shroud on the top of ground. The gas was then piped into a gas processing unit, condensed into liquid waste and collected in another unit for recycling or incineration.

In-situ stream/hot air stripping eliminates the need for any excavation of the contaminated soil and is not limited, as many traditional technologies are, by soil conditions such as particle size, initial porosity, chemical concentration, or viscosity (15).

(3). Activated carbon adsorption:

The effectiveness of activated carbon as a treatment process is due to its ability to adsorb molecules dissolved in water. One of the most desirable aspects of activated carbon adsorption as a treatment process is its ability to remove contaminants to very low levels. Activated carbon comes into two forms, granular and powdered. The granular form of activated carbon is commonly used in treatment of contaminated groundwater. Highly soluble compounds are not as readily removed by granular activated carbon as less soluble ones. Contaminants with high molecular weight are more readily adsorbed than lighter contaminants (12)

1.3 PCSs IN HOT MIX ASPHALT CONCRETE

1.3.1 Hot Mix Asphalt

Hot mix asphalt(HMA) consists of a combination of aggregate uniformly mixed and coated with asphalt cement. To dry the aggregates and to obtain sufficient fluidity of asphalt cement for proper mixing and workability, both the aggregate and asphalt must be heated prior to mixing. Aggregates and asphalt are combined in a mixing facility in which all of the constituent material is heated, proportioned, and mixed to produce the desired paving mixture. In a batch-mixing facility, hot asphalt mixtures are produced using a feed system, an asphalt proportioning system, a aggregate dryer, and a storage silo (Figure.1) .

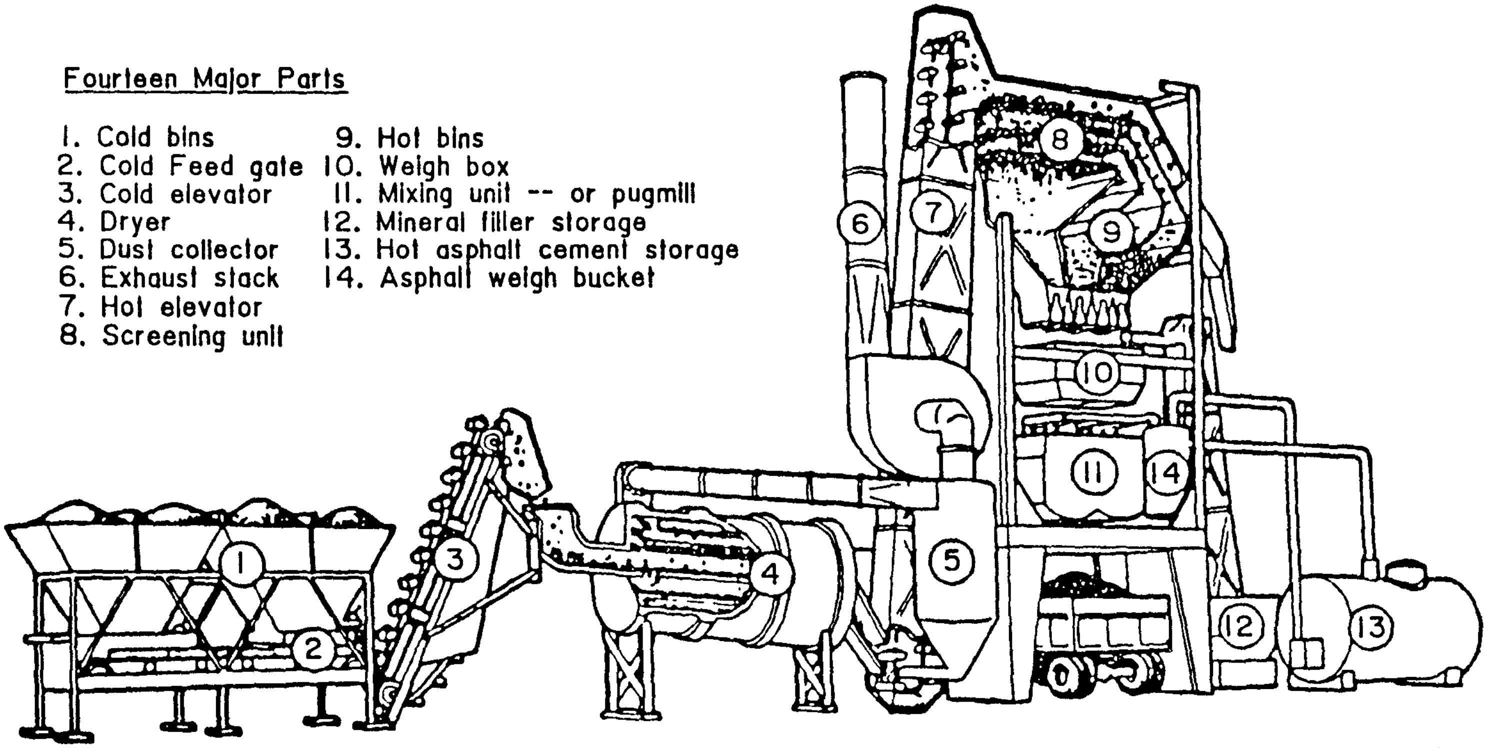


Figure 1. Schematic Representation of Hot Mix Asphalt Plant

Little is known about the release of VOCs during the production of regular HMA. The industrial Environmental Research Laboratory of EPA had developed a quantitative method to estimate the emission of VOCs from HMA plants in 1981. Their study was carried out by field sampling of five HMA plants under a variety of operating conditions, included in those plants was a plant that processed a mixture of recycled pavement and virgin aggregate, and a plant that employed a wet scrubber. The results showed that VOCs emissions from HMA plants are on the order of 0.1 to 0.4 pounds of VOCs (as carbon) per ton of asphalt concrete produced. VOCs emissions appeared to be independent of operating parameters, over the normal range of plant operation and within the limited scope of the statistical testing employed. It appears that a wet scrubber reduced VOCs emissions. The nationwide emission of VOCs from all HMA plants was estimated to be about 20,600 tons per year (16). In another survey by office of air quanlity planning and standard of EPA, the emission factor for VOCs from stacks of asphalt plants was estimated to be 0.028 lb/ton (25).

1.3.2. Solidification and Reuse by Adding PCSs to HMA

Solidification and binding processes have developed from man's attempt to better transportation or navigation. In ancient times(3,000 B.C) the Chinese Dschou dynasty had several roads constructed for transportation of goods (17). The Roman port of Cosa (2nd century B.C) utilized mortar called pozzolana for harbor protection (17). Solidification is the process which solidifies the hazardous chemicals in PCSs into the solid phase, thereby preventing interphase transfer into aqueous, gaseous and other mobile phases in the soil environment. It reduces the rate of contaminant releases from the soil, so concentrations along exposure pathway are held within acceptable limits.

Waste treatment by asphalt solidification can be traced back to disposal of low level radioactive waste in the 1950s. As a thermalplastic material, asphalt was evaluated to provide more consistency, lower weight, and better space efficiency (18). In processing radioactive wastes with asphalt, the wastes is dried, heated and dispersed through a heated, plastic matrix. The mixture is then cooled to solidify the mass. Later, asphalt was adapted for handling industrial wastes. One innovation that a number of highway agencies have looking at is how various solid-waste materials could be used in the construction of asphalt pavements. Incorporating scrap rubber from old tires in asphalt pavements has received the most attention (19). Asphalt concrete containing additives like rubber, plastics can be made for special uses like tennis courts and running tracks. Another study showed asphalt also can be used to stabilize organic compounds. Waste Chem's asphalt encapsulation technology can reduce semivolatile organic compound concentrations in the toxicity characteristic leaching procedure (TCLP) extracts of treated wastes (20).

The major advantages of HMA technique can be summarized as follows:

(1). Contaminant migration rates are generally lower for solidification of contaminants using asphalt than for most other stabilization techniques, so it is able to solidify very soluble, toxic materials.

(2). Asphalt mixture is fairly resistant to attack by most aqueous solutions.

(3). Asphalt adheres well to incorporated materials. Therefor, the final product has good strength.

(4). Asphalt pavements make up more than 90% of the paved road in the U.S, so there are no problem for use of asphalt mixture with PCSs.

The disadvantages of this technique are:

(1). There is a increase in total volume after this process.

(2). High concentration of volatile products such as gasoline should not be present in the PCSs as processing such materials can cause fire.

1.3.3 Technology of Mixing asphalt with PCSs

One recently proposed remedial option for PCSs involves the incorporation of PCSs into

HMA as a partial substitute for stone aggregate; the mixture is then used for paving. In this process, aggregates mixed with PCSs are heated and dried, then they are mixed thoroughly with hot asphalt to form the final product.

The primary mechanisms of remediation in this process are volatilization and thermal destruction by incineration. During this process, PCSs is passed through a rotary dryer to remove volatile compounds and moisture where average temperatures range from 260 to 427°C. There is partial incineration of volatile organic com- pounds during the process. Solidification or encapsulation is a secondary mechanism of PCSs remediation that serves to contain heavier hydrocarbon fractions that might not be removed during the process. Lighter petroleum hydrocarbon contained in PCSs are incompatible with asphalt as these compounds can act as solvents to soften the final asphalt product. When PCSs are utilized in HMA plants, the soils are simply added to the aggregate feed stream as a small percentage of total feed. A restriction of PCSs feed is required in order to maintain final product quality and to minimize the danger of air emissions caused by volatilization of the hydrocarbon compounds.

In Massachusetts, the Henley-Lundgren Company was allowed to use PCSs as part of their aggregate feed by the Massachusetts Department of Environmental Quality Engineering. The PCSs was incorporated at less than 5 % by weight of the total feed. Even at this small percentage, this plant has the capacity to reuse 8000 tons of PCSs annually (21). Processing PCSs in HMA plants has several advantages: The incineration technology required is related to HMA technology; the capital investment is in place, and only minor modifications required. The decontaminated soil can be incorporated into HMA, and small percentages of PCSs in HMA can be economically processed large quantities. George Brox Inc., in Massachusetts modified the HMA plant such that a rotating ceramic cylinder was inserted between the burner and the dryer was used as a combustion chamber. PCSs entering this ceramic cylinder immediately flashes off its water and hydrocarbon into the 2000°F flame and 95 % hydrocarbons were destroyed without increase VOCs emissions from HMA plant (22). American Reclamation Corporation in Massachusetts developed a cold mixing process for incorporation of PCSs into asphalt concrete. Their tests confirmed that the petroleum contaminants in the soil was combined with the asphalt to produce a mixture that will not separate and will not release the oil back into the environment (23).

A national survey found five states had experience with the reuse of PCSs by adding it in HMA. In Massachusetts, this method is now considered to be the most favored option for disposal of PCSs.

Presently, it is only assumed that high temperature encounted in the dry mixer and secondary stabilization of the PCSs within asphalt mixture provides ade-quate remediation measure. The research in this thesis investigated the air emission during mixing PCSs with asphalt and the rate of releasing hydrocarbons to environment after the solidification process.

Chapter 2
RESEARCH OBJECTIVE

2.1. Determination of Volatile Organic Compounds Emitted from Hot Mixing Asphalt with PCSs

VOCs emissions during treatment of hazardous waste treatment represent a major source of organic contaminants entering the atmosphere. These emissions affect worker health and air quality. Acute health effects occur from exposure to a pollutant over a short time period. These effects include neurotoxicites, dermatological problems, and respiratory difficulties. Chronic health effects result from long term exposure to pollutants at comparatively low concentrations. Carcinogenity, mutagenity, and teratogenicity are the most common measures of chronic effects.

The petroleum contaminated soils due to leaking underground storage tanks are required to be removed and isolated in a designated area for asphalt incorporation treatment. Due to partial incineration and volatilization of organic compounds, some organic compounds were emitted during the mixing process. Measuring total VOCs is not good enough to evaluate the toxic effect of different organic compounds, so a broad spectrum approach using thermal desorption techniques was used to monitor the VOCs emission (24)(25). The organic compounds chosen for monitering were found in soil and groundwater and were included in The Hazardous Substance List (Table 1).

The air sampling and analysis system is based on solid adsorbent sampling tubes, thermal desorption and gas chromatographic analysis (24). The collection of VOCs was twice condensed in cryogenic traps to improve capillary column resolution. Before cryogenic refocusing, a purge step serves to remove any oxygen remaining in the tube. This eliminates the problem of the solid adsorbent reacting with the oxygen when heated, and also removes traces of water from the tube.

Table.1. Properties of Examined VOCs Included within The Hazardous Substance List

Compound	Molecular weight (g/mol)	Boiling Point (°C)	Vapor pressure (mm)	Aqueous solubility (mg/L)
Chloromethane(CM)	51	-24	3800	4000
Chloroform(Clfo)	119.4	62	160	8000
1,2-Dichloroethane(1,2-D)	99.0	83.5	61	8690
1,1,1-Trichloroethane (1,1,1-TCE)	133.4	71-81	100	4400
Trichloroethene(TriC)	131.5	86.7	60	1100
Benzene(Bz)	78.1	80.1	76	1780
Perchloroethene(PerC)	165.8	121.4	14	150
Toluene(Tol)	92.1	110.8	22	515
Ethylbenzene(EB)	106.2	136.2	7	152
m-Xylene(m-X)	106.2	139	6	
o,p-Xylene(o,p-X)	106.2	144.4	5	175

* Properties are at 20°C

Air samples from two asphalt plants were tested; one is a regular asphalt plant in Newark, another modified asphalt plant in New Hampshire which incorporates PCSs into hot asphalt. In both asphalts plant, air pollution control device is baghouse.

2.2 LEACHING TEST FOR ASPHALT MIXED WITH PCSs

The increased number of organic contaminants being detected in ground waters is causing concern because of potential health risks claimed to be associated with human exposure to these substances. Soil contaminated with petroleum oil is a potential threat to both surface water and groundwater, thus a key issue is whether hydrocarbon chemicals will leach out of the asphalt mixture when it is disposed to pave roads. A uniform leaching test was used to estimate the quality of leachate that would be produced by the asphalt mixture (26).

The leachability test was designed to simulate the rate of contaminants release when HMA with PCSs are exposed to the actual environment in which they were be used. The test methodology and test standards were developed in cooperation with the New Jersey Department of Environmental Protection and Energy (NJDEP). The experimental protocol evolved based on the information and experience of EPA toxicity characteristics leaching procedure (TCLP) and waste stabilization/solidifica- tion program(27)(28), the waste solidification program of the US Army Corps of Engineers, and the nuclear waste research program at Brookhavan and Oak Ridge National Laboratories.

The uniform leaching procedure gives an indication of the amount of each element that is leachable under specific experimental conditions (29)(30). The structural integrity of sample was kept in the test, since particle size reduction would be inappropriate in those instances where solidification of the waste is needed to meet the best demonstrated available technology provision of environmental law. Grinding may integrity of sample was kept in the test, since particle size reduction would be inappropriate in those instances where solidification of the waste is needed to meet the best demonstrated available technology provision of environmental law. Grinding may not adequately represent the actual process. Particle reduction alters the physical character of many solidified wastes by destroying the cementitious property of these wastes in such a way that the leaching rate may increase unrealistically.

Chapter 3
EXPERIMENTS

3.1 VOCs EMISSION TEST

3.1.1 Air Sampling and Analysis

Samples from stack of hot mixing asphalt plant were collected by drawing a volume of air through a 1/4" stainless cartridges packed with 1.5 g of 60/80 mesh Tenax TA using a air sampling pump (Figure 2). Samples were drawn at 250-500 ml/min. The tubes were desorbed using a Tekmar modal 5010 Automatic Desorber connected to a Varian 3400 GC with a flame ionization detector. Both systems were interfaced so as to automate the entire analysis (Figure 3).

The desorption conditions are as follows:

Prepurge: 5 min, at 10 ml/min
Desorb: 8 min , 210 °C, at 10 ml/min
Cryotrap 1: -150 °C
Cryotrap 2: -150 °C
Transfer: 10 min, 210 °C
Inject: 0.75 min, 210 °C

The column used for GC/FID analysis was crosslinked methylsilicone gum, 50 m x 0.2 mm x 0.5 um film thickness.

Flow rate:
Hydrogen = 30 ml/min
Air = 300 ml/min
Carrier gas(helium): 1 ml/min
Make-up gas: 30 ml/min

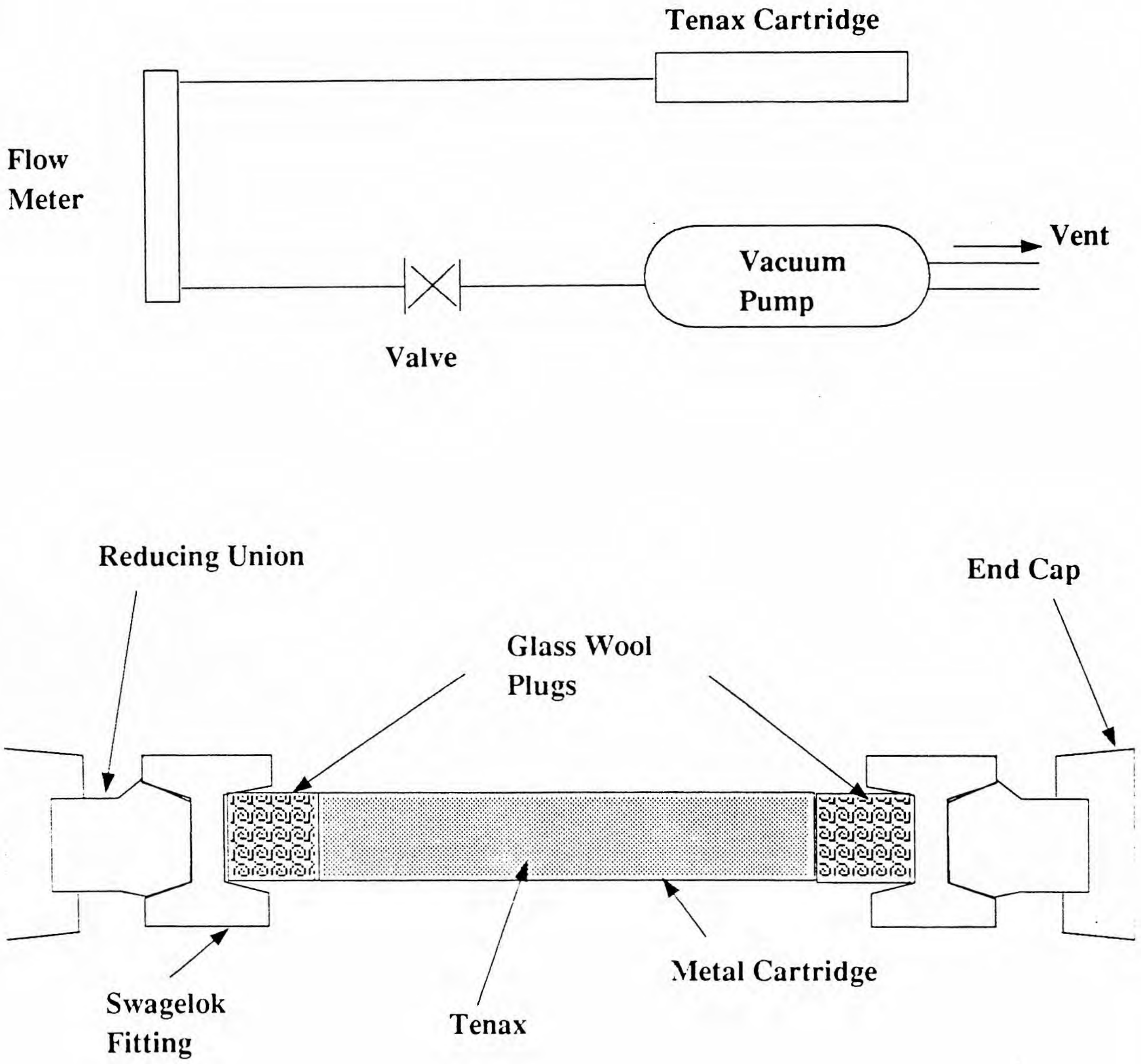


Figure 2. Sampling System and Tenax Tube

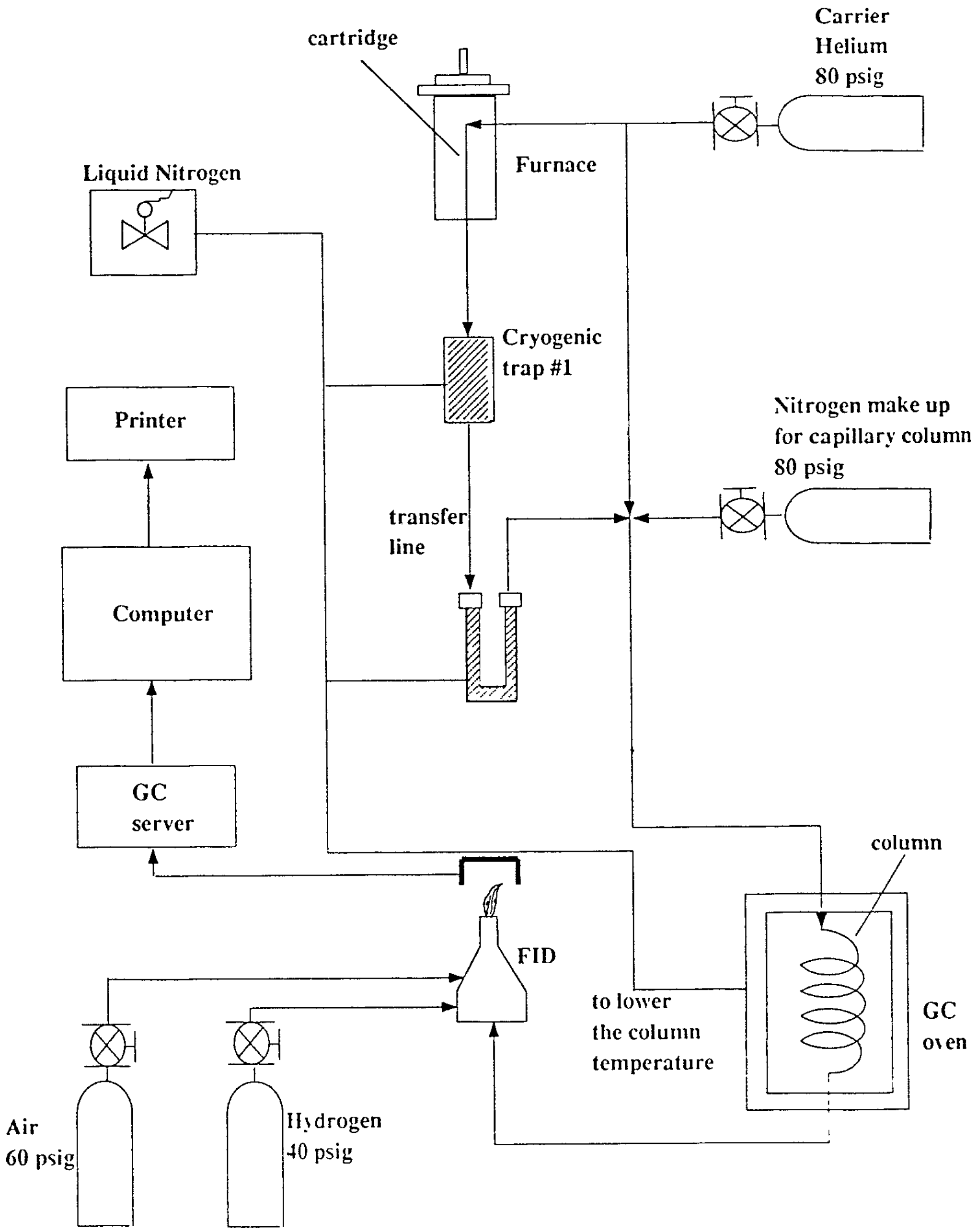


Figure 3. Schematic Representation of The Chemical Analysis

The temperature program consisted of initial temperature of 15 °C for 8 minutes, and then program increase to 210 °C at 4 °C/min.

Prior to sample collection, the sampling flow rate was calibrated over a range including the rate to be used for sampling. The flow rate was checked before and after each sample collection. Each time, the following parameters were recorded: date, sampling location, air temperature, flow rate, collecting time, tube number. The samples were stored under 4 °C temperature and analyzed within one week after sampling. The Tenax cartridge were baked for 24 hours at 250 °C under an inert gas purge (20-30 ml/min) before being used.

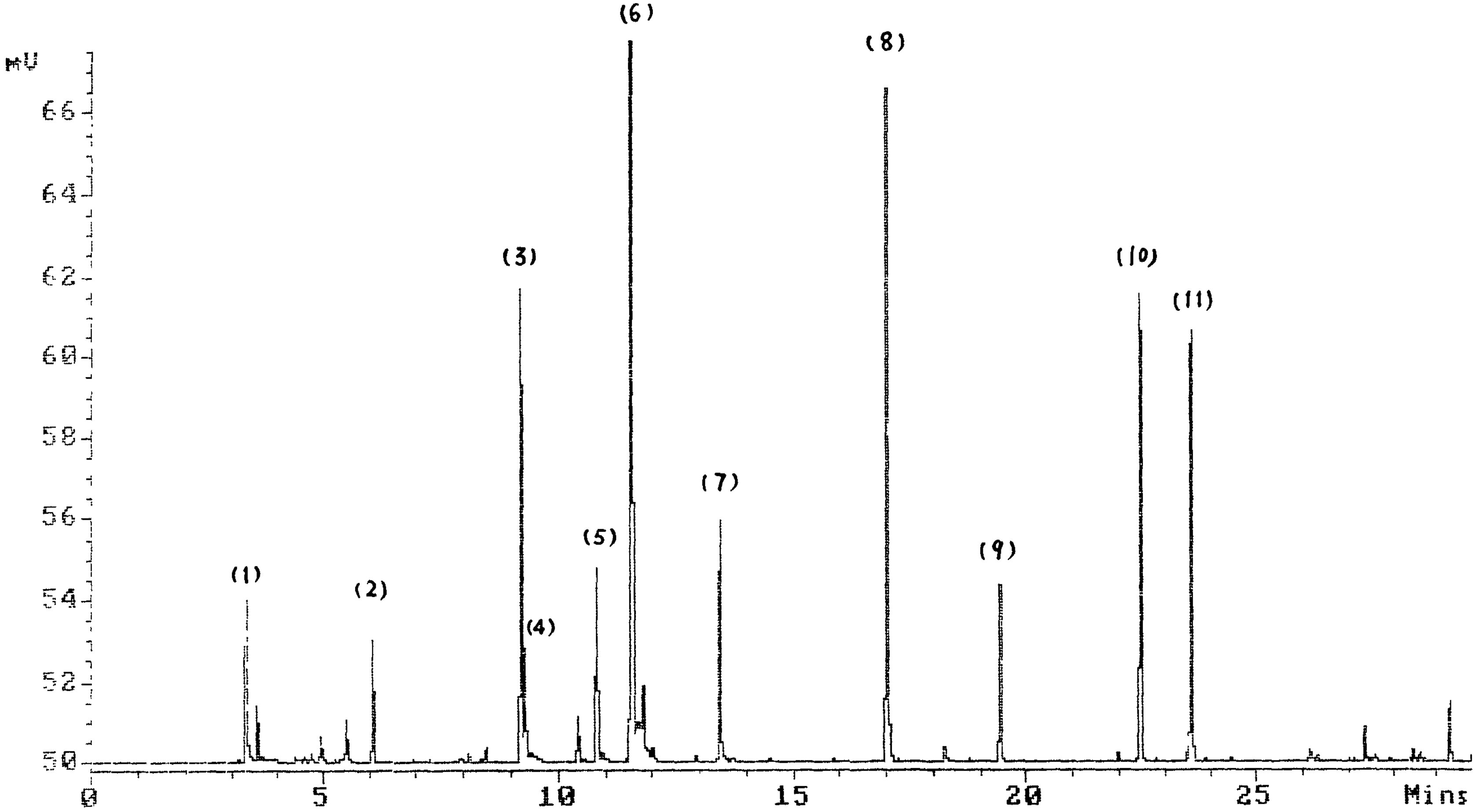
The standard gas was prepared from a mixture of target compounds: Chloromethane, Dichloromethane, Hexane, Chloroform, 1,1,1-trichloroethane(1,1,1-TCE), Benzene, Trichloroethylene, Toluene, Perchloroethylene, p,m-Xylene, o-Xylene (Figure 4).

The compounds were injected into an evacuated and clean 13 liter stainless steel cylinder with zero grade helium. The analysis of the standard was performed by Alphagaz, Morusvelle, PA.

External standards were used to calculate the response factor of each compound every week. The process involved analysis of four calibration levels for each compound. If the instrumental response was linear over concentration range of compounds a linear equation can be employed : $Y = A + B x$. The limit of detection (LOD) and limit of quatitation(LOQ) were defined as (31):

$$LOD = A + 3.3\ S \qquad LOQ = A + 10\ S$$

where A is the intercept of the above equation, and S is the standard deviation of replicate determinations of the lowest concentration level.



(1). Chloromethane, (2). Dichloromethane,(3). Hexane, (4). Chloroform, (5). 1,1,1-Trichloroethane, (6). Benzene, (7). Trichloroethylene, (8). Toluene, (9).Perchloroethylene, (10). p,m-Xylene, (11). o-Xylene.

Figure 4. The Gas Chromatogrph of Gas Standard Used for Emission Test

3.1.2 Measurement Total Non-methane Organic Compound(NMOC)

NMOC measurement was obtained by summing up the concentrations of individual species. The cryogenic sample preconcentration greatly increases the sensitivity of the method because it effectively minimizes interference from methane and oxygen. The computer program MINICHROM allows analysis information for GC air sample to be placed to a file that can then be read into Lotus 1-2-3. Once Lotus 1-2-3 displays the file as a spreadsheet, The MANIPULATE and REPORT commands in Lotus 1-2-3 can be used to sum up and report the total area of individual compounds.

The NMOC calibration curve was prepared by using a propane standard. In this experiment, 10 ppm of propane in helium air was used with a gas-tight syringe at the maximum pressure of the gas-tight injector was 250 psi. The pressure of standard chosen ranged from 14.4 to 30 psi. The concentration unit is parts per million carbon (ppmC) which is equivalent to parts per million by volume (ppmv) multiplied by number of carbon atoms in propane (32).

3.2 Leaching Test

3.2.1 Leaching medium:

The leaching medium chosen was reagent water with a pH value of 6.8 at temperature of 25 C. Since the asphalt mixtures were disposed on the surface of ground, the reagent water should be more representative of the actual environmental than an acidic leaching medium. The reagent water was prepared by boiling deionied water for 15 minutes. Subsequently, while maintaining the water at about 90 °C, nitrogen gas was bubbled through the water for one hour.

3.2.2 Sample preparation:

The sample was treated as a monolithic waste; i.e., the sample was not pulverized prior to testing. The asphalt concrete with PCSs were compacted to 2" x 2" x 2" size before being tested.

The aggregate sizes are:

1. between 1 inch and 1/2 inch.
2. between 1/2 inch and 1/4 inch.
3. between 1/4 inch and 1/8 inch.
4. between 1/8 inch and #10 sieve.
5. sand passing #10 sieve.
6. dust passing #10 sieve.

Procedure of sample preparation:

(1).Heating asphalt at temperature 320 °C.

(2).Preheating mixer at 130 °C for method I; at 195 °C for method II.

(3).Mixing the hot aggregate with soil in dry mixer for one minute and then add the asphalt cement in dry mixer and mixed for another minute.

(4).Pouring the mixture into a compation mold and compacting the mixture.

Six PCSs from New Jersey were used in the test. The degree of contamination of these six PCSs was showed in table 2. From previous Marshall tests (33), and the optimum asphalt concentration for the six PCSs were determined as follows:

PCS #1: 4.5 %	PCS #2: 4.5%
PCS #3: 5.0 %	PCS #4: 4.25 %
PCS #5: 4.5 %	PCS #6: 4.5 %

3.2.3 Leaching procedure:

The compacted asphalt samples with PCSs were placed in glass containers of volume 480 mililiters and sealed with Teflon septum caps. The volume of the container was at least three times larger than the size of the sample, so sufficient space was available in the container and the sample was surrounded on all side by leaching media. There was zero

Table 2. Soil Data for Six Contaminated Soils from New Jersey

	Soil Type					
	PCS #1	PCS #2	PCS #3	PCS #4	PCS #5	PCS #6
Soil Classification	Well graded	Clayey silt	Silty sand	Poorly graded	Silty clay	Poorly graded sand with silt
In Situ Moisture Content (%)	7.3	14.3	24.7	14.4	19.6	10.1
Level of Contamination	0.11% Heating oil	0.12% Heating oil	0.66% Heating oil	25 ppm Gasoline	1500 pm Gasoline	330 ppm Gasoline

head space to minimize the effects of volatilization. The containers were placed on a shaker for a period of 96 hours. After the end of that period, the containers were opened and 25 ml water sample was immediately drawn using a gas-tight syringe. Long term leaching of contaminant for PCS #3 sample was investigated using leaching duration of one day, one week and one month.

3.2.4 Analysis procedure:

The analysis system used the ALS 2016 and Tekmar 2000 purge & trap concentrator interfaced to a Varian 3400 GC with FID detector.

Parameters of ALS 2016 were as follows:

Preheat: 2 minutes
Purge: 15 minutes, helium flow: rate 40ml/min
Dry purge: 4 minutes
Cool down: -150 °C
Desorb preheat: 150 °C
Desorb: 5 minutes at 180°C
Inject: 3 minutes at 190 °C
Bake: 10 minutes at 240 °C

The GC parameters were as follows:

Initial column temperature: 40 °C
Initial column hold time: 5 minutes
Program 1 final column temperature: 65 °C
Program 1 column rate: 2 °C/min
Program 1 column hold time: 0
Program 2 final column temperature: 190 °C

Program 2 column rate: 8 °C/min

Program 2 column hold time: 5 minutes

Inject temperature: 210 °C

Detect temperature: 250 °C

External standard was used for calibration. The standard was prepared using a mixture of target compounds in methanol: Dichloromethane, 1,2-Dichloroethane, 1,1,1-Trichloroethane, Hexane, Benzene, Toluene, Perchloroethylene, Ethyl-benzene, p,m-Xylene, o-Xylene (Figure 5).

3.2.5 Quality control:

The major source of interferences is cross contamination of samples. To prevent the cross contamination, reagent water blank was run twice before running each sample to demonstrate that interferences from the analytical system were under control.

The following procedure was used to clean up the vials and glass containers.:

(1). Wash the vials and containers thoroughly in hot tap water and detergent to remove particulate matter and gross contaminants.

(2). Rinse thoroughly with tap water.

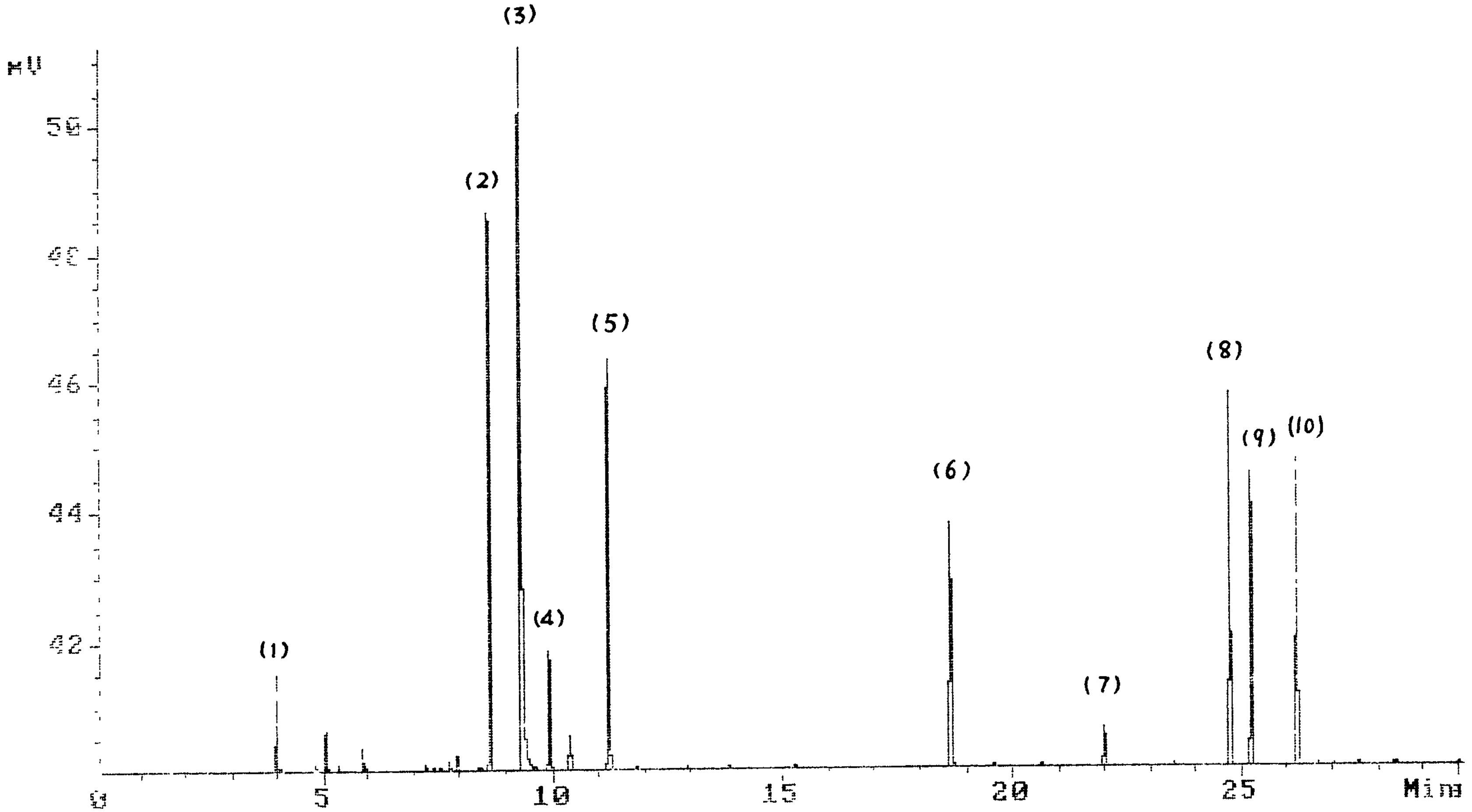
(3). Rinse three times with deionized water.

(4). Place in a vacuum oven at 105 °C for 12 hours to bake off all volatile compounds.

(5). Cool for 30 minutes, screw the lids on tightly and store in an area not subject to contamination by air or other sources.

To assess the precision of the measurements, three samples were injected for each concentration level and were analyzed to get the mean and standard deviation. Seven standard samples with same concentration were analyzed to get the coefficient of variation (CV) for assessing the reproducibility of this method.

The detection limit of the method (MDL) is defined as the minimum concen-



(1). Dichloromethane, (2).Hexane, (3). 1,2-Dichloroethane, (4). 1,1,1-Trichloroethane, (5). Benzene, (6). Toluene, (7). Perchloroethylene, (8). Ethylbenzene, (9). p,m-Xylene, (10). o-Xylene.

Figure 5. The Gas Chromatograph of Standard for Leaching Test

tration of a substance that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero and determined from analysis of a sample in given matrix containing analyte compounds. In this test, reagent water was used to estimate the MDL concentration. A standard (analyte in reagent water) at concentration equal to 1 to 5 times of the estimated MDL was used to calculate the MDL. The MDL was reported in concentration units as the standard deviation (S) of the replicates multiplied by the appropriate Student's t-value (for a one-tailed test at 99% confidence) for the number of replicates (34). In this test, the number of replicates was seven, so MDL is defined as:

$$\text{MDL} = 3.143 \times S$$

Each day, 3-4 samples were spiked with at least 10% of the samples and analyzed to monitor and evaluate the experimental data quality. The percentage recovery was calculated using the following equation:

$$P = 100\,(A - B)\% \,/\, T$$

where A is concentration after spiking, B is the background concentration. T is the known true value of the spike.

After the analysis of ten spiked samples, the average percentage recovery (P) and the standard deviation of the percentage recovery (Sp) values were calculated and expressed as P +/- Sp.

Chapter 4
RESULTS AND DISCUSSION

4.1 VOCs EMISSION TEST

4.1.1 Reproducibility and detect limit

In this experiment, ten Tenax cartridges were spiked with known quantities of standard and then desorbed into the analytical system. The reproducibility can be expressed using the coefficients of variation (CV) for each target compound. For most of target compounds, the coefficients of variation ranged from 6.7 % to 21.4 % ; LOD values ranged from 0.026 to 0.54 ppb and LOQ values ranged from 0.089 to 1.80 ppb. The LOQ values were much lower than concentration of the air sample.

4.1.2. Breakthrough test

Each time, backup cartridges (two Tenax cartridges in series) were used to measure breakthrough percentages of each compound (35). All backup cartridges contained less than 10 % of the amount of compounds in the front cartridges, except in two cartridges where benzene break through was 10.8 % .

4.1.3 VOCs emission from normal HMA plant

VOCs concentration was measured from the stack of a normal HMA plant in New Jersey where six air samples were taken. The results are showed in table 3.

4.1.4 VOCs emission from mixing asphalt with PCSs

VOCs emission was measured from stack of asphalt plant which processed hot asphalt with PCSs in New Hampshire (Figure 6). The samples were taken four times. The interval of each time was 15 minutes. Four samples were taken each time. The average concentrations are shown in Table 4 (Figure 7(a), 7(b)).

Table 3. VOCs Concentration from Stack of Regular HMA plant

Compound	Concentration (ppbv)	Background
Chloromethane	162.83	7.34
Dichloromethane	109.47	3.21
Hexane	149.39	ND*
Chloroform	173.66	2.45
1,1,1-trichloroethane	81.76	1.64
Trichloroethylene	133.06	ND
Toluene	24.19	1.48
Benzene	131.54	2.10
Perchloroethylene	113.06	ND
p,m-Xylene	16.82	1.04
o-Xylene	5.87	0.84

*: No detect means lower than detect limits

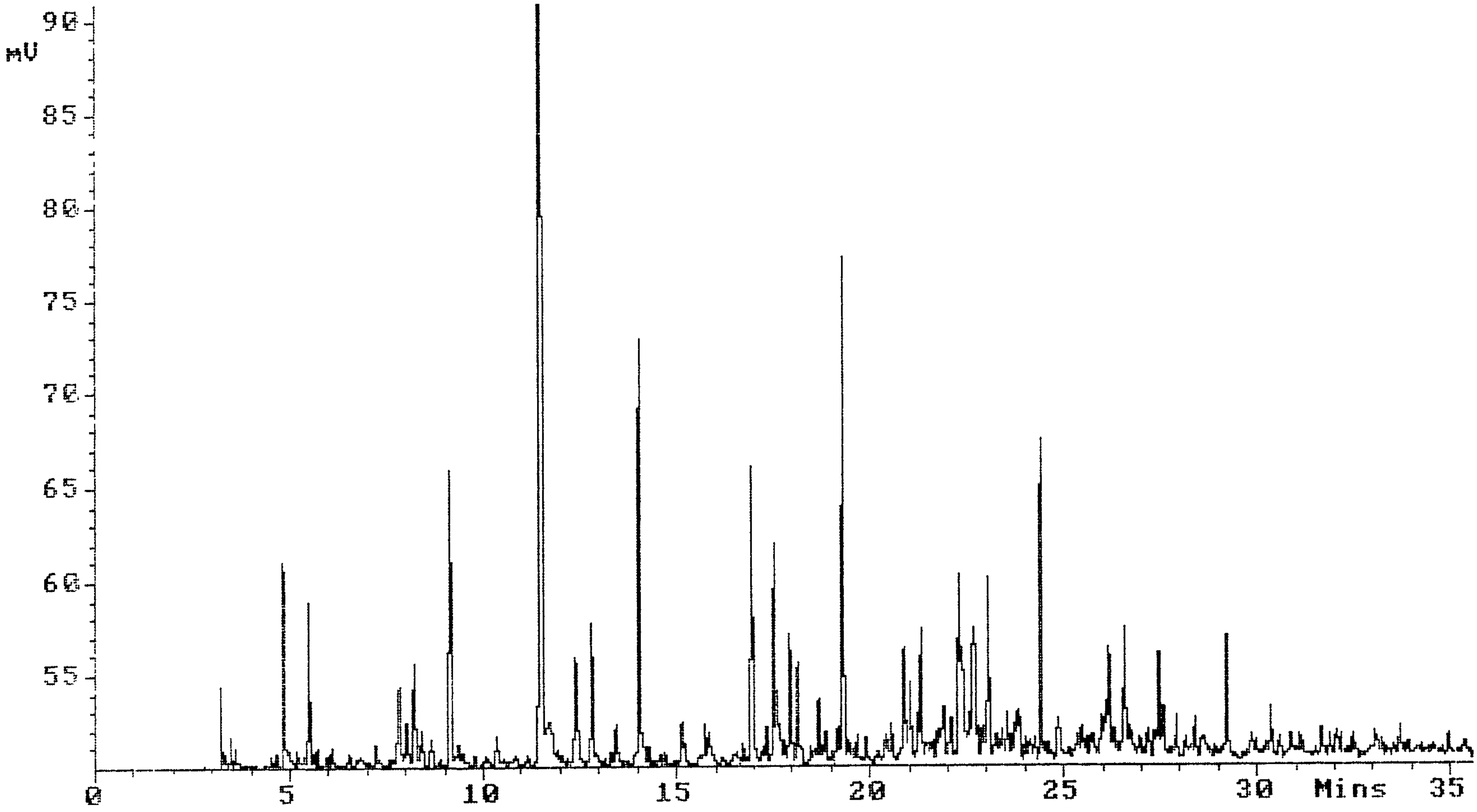


Figure 6. The Chromatogram of Air Sample from Mixing Asphalt with PCSs

Table 4. VOCs Concentration from Mixing Asphalt with PCSs

Compound	Concentration (ppbv)	Environmental control
Chloromethane	1056.44	17.14
Dichloromethane	481.37	2.14
Hexane	283.45	ND
Chloroform	1092.11	ND
1,1,1-trichloroethane	274.72	2.28
Trichloroethylene	364.88	ND
Toluene	366.16	4.84
Benzene	542.46	ND
Perchloroethylene	292.14	3.96
p,m-Xylene	88.23	1.96
o-Xylene	99.13	2.46

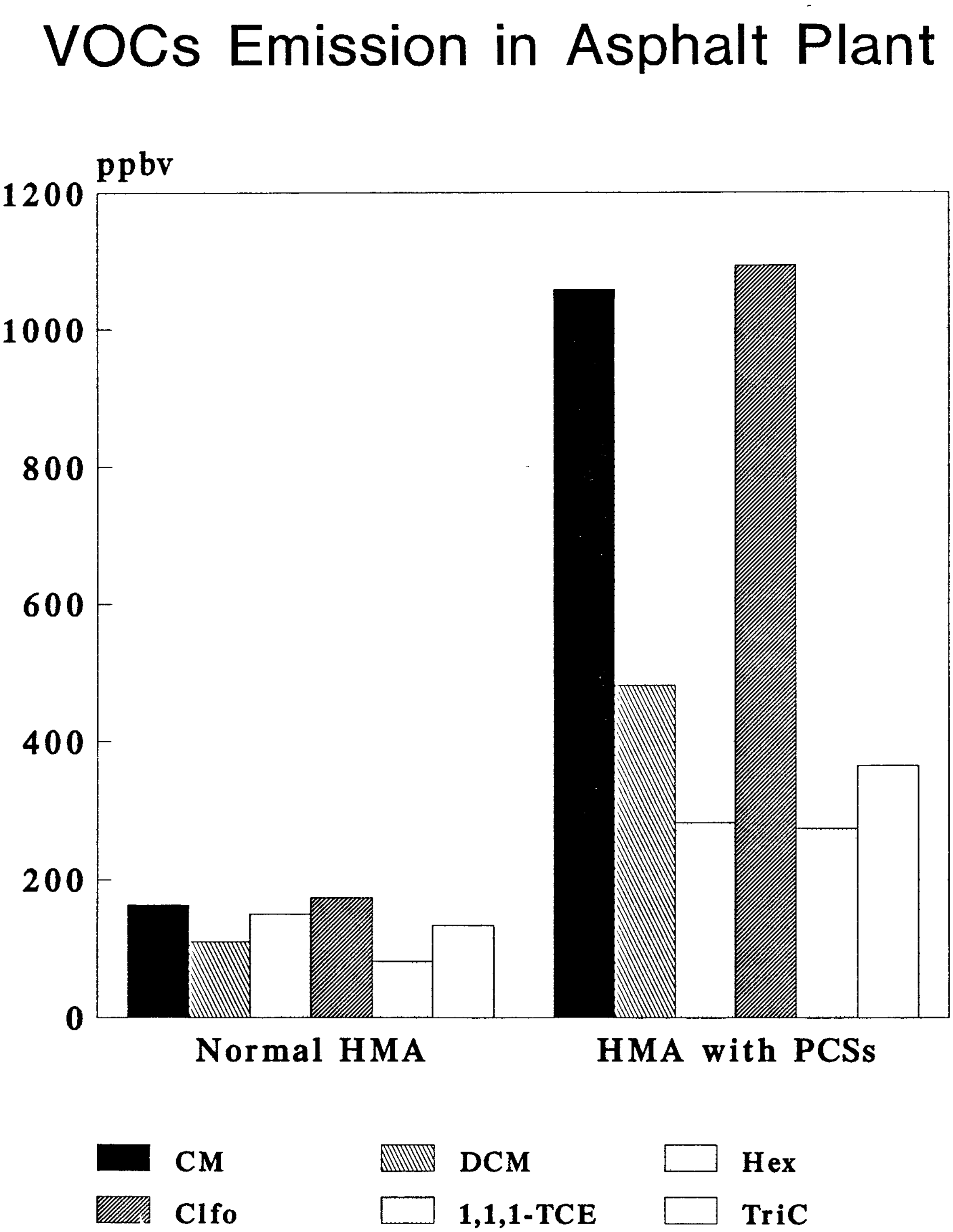


Figure 7 (a). Comparison of VOCs Emission between Regular HMA Plant and HMA Plant Which Incorporated PCSs (1)

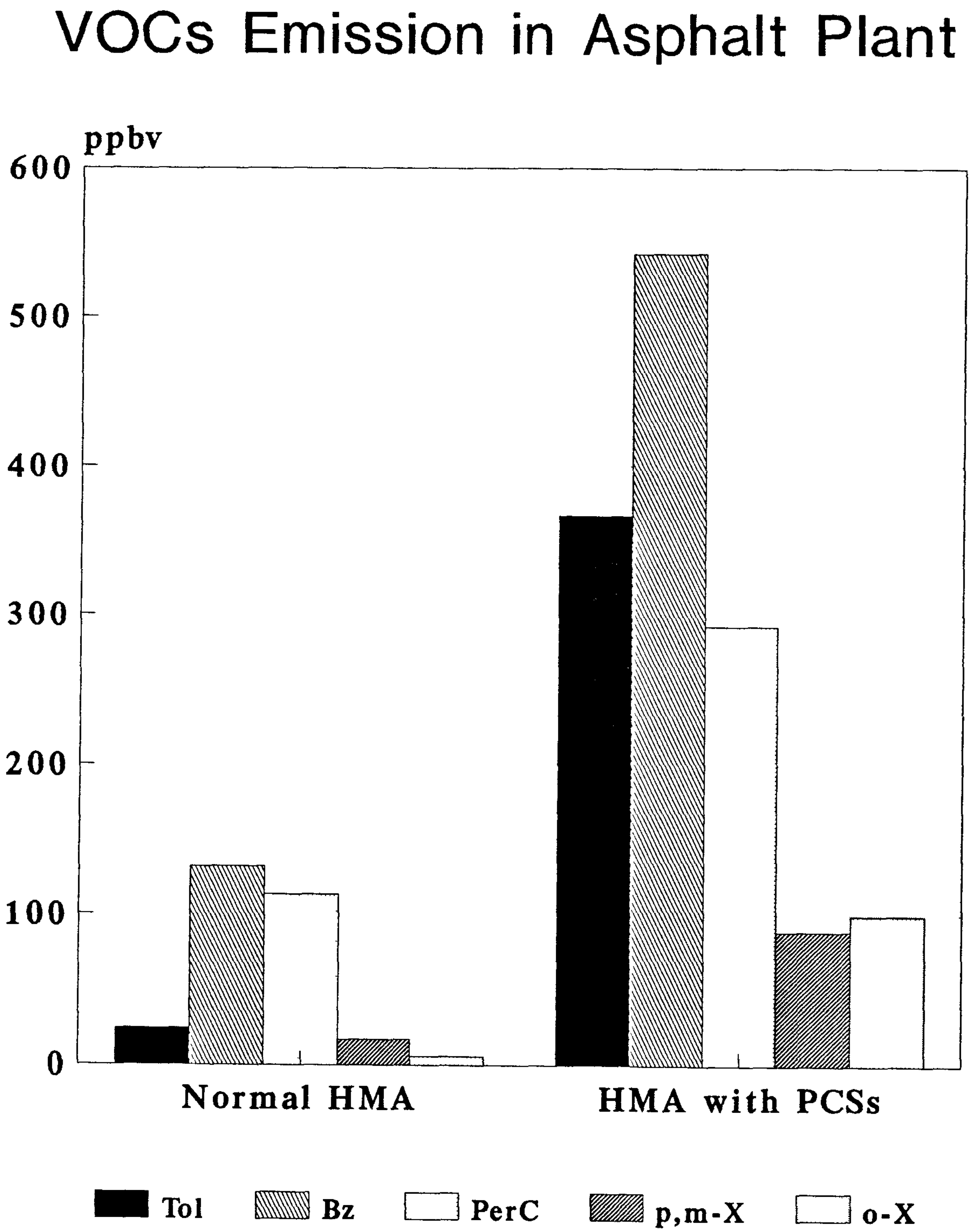


Figure 7(b). Comparison of VOCs Emission between Regular HMA Plant and HMA Plant Which Incorporated PCSs (2)

4.1.5 Emission Factor of NMOC

Emission factor can be calculated by the NMOC concentration of the stack (Figure 8):

(1). Conversion of PPMC to pounds carbon of NMOC per hour

Data:	NMOC concentration of the stack
	Flow rate of stack gas(dry standard cubic feet per minute)
	Production rate of asphalt mixture(tons per hour)

Constants: Molecular weight of carbon = 12.01

Standard molar gas volume = 386 cubic feet(21°C)

$$\frac{\text{lb.}}{\text{hr}} = \frac{\text{Concentration of stack}}{100{,}000} \times \frac{12.01}{386} \times \text{gas flow rate} \times 60$$

(2). Conversion of pounds carbon per hour to pounds carbon per ton asphalt mixture

$$\frac{\text{lb. carbon}}{\text{ton}} = \frac{\text{lb carbon}}{\text{hour}} \div \text{prouction rate}$$

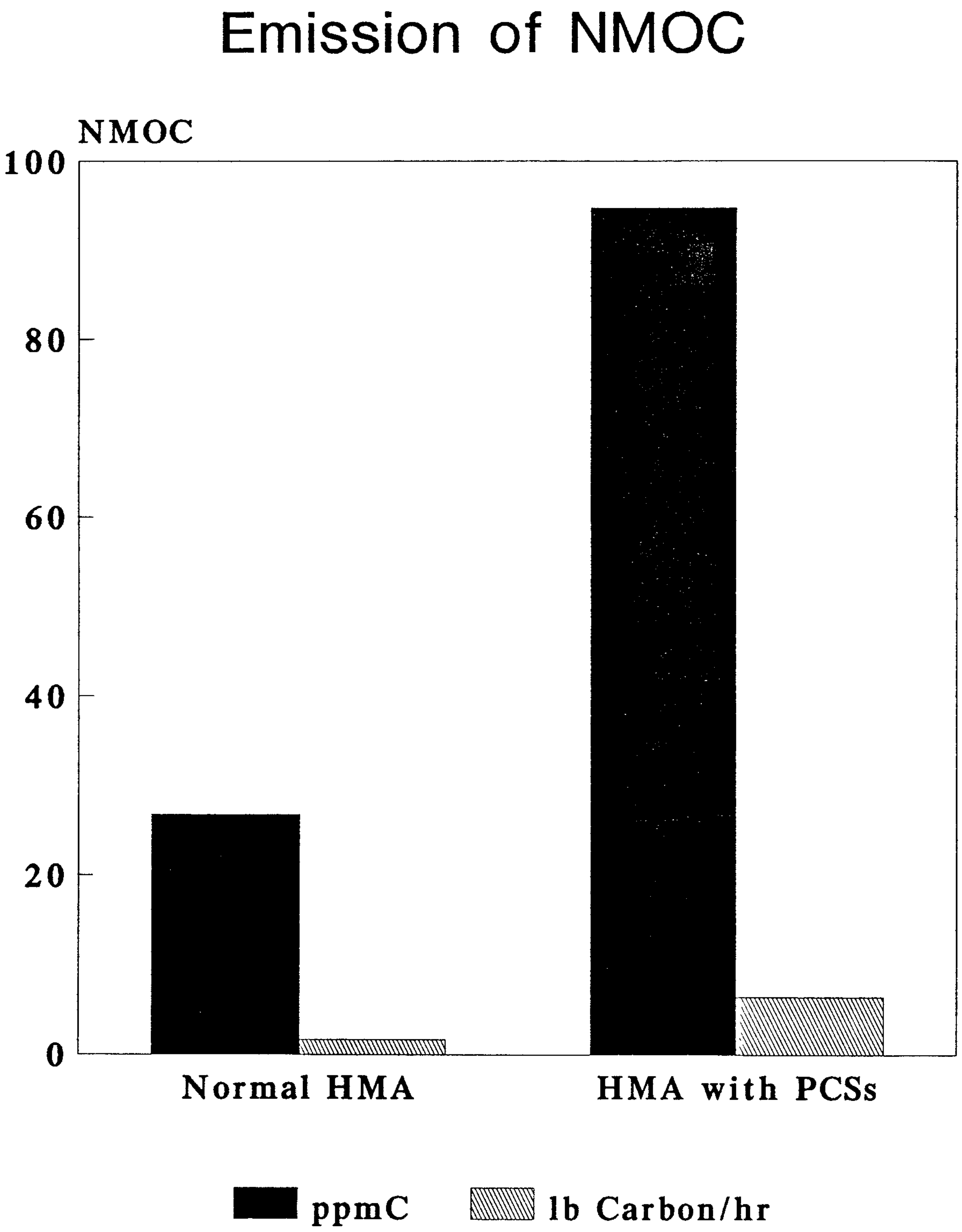


Figure 8. Comparison of NMOC Emission between Regular HMA Plant and HMA Plant Which incorporated PCSs

Table 5. NMOC Emissions from Two Asphalt Plants

	Concentration	Emission factor	
	(ppmc)	(lb carbon/hr)	(lb carbon/ton)
Regular asphalt plant	26.74	1.71	0.017
Asphalt plant mixing PCSs	94.75	6.50	0.065

4.1.6 Discussion

4.1.6.1. The level of volatile organic compounds from stack of asphalt plant is a subject of intense interest when mixing contaminated soil with hot asphalt. Monitoring of these compounds can be accomplished by collection in Tenax cartridge, then thermal desorption and GC separation. This method is sensitive and relatively precise. The reproducibility of this method was determined by the coefficient of variation that was under 30 % , and hence it is a reasonable method to measure a wide variety of volatile compounds from asphalt plant. It is very important to accurately measure the volume of air stream sampled in order to determine the emission factor.

4.1.6.2. In asphalt plant, there are toxic organic compounds emitted from the stack. For individual compound, the concentration did not approach levels that cause severe health effects, however the asphalt plants may emit chemical mixture consisting of several compounds with similar health effects, such as carcinogenic and mutagenic effects. If the cumulative health effects of these compounds are assessed, the combined exposure should exceed threshold levels. Health effects due to Exposure of complex mixture will probably be most significant when adding large amounts of PCSs into asphalt concrete.

4.1.6.3. Processing contaminated soil in HMA is a new recycling technique. This method has several advantages. The main advantages are: 1. It offers partial incineration for the organic compounds. 2. There is some solidification of organic compounds of heavier molecular weight. and 3. Petroleum in the contaminated soil can be used as a part of fuel in the drying process. The most important aspect of our research was the amount of the volatile compounds driven off during the mixing and increased VOCs emissions. Based on a pilot-scale study, nearly 10 to 60 percent of volatile were emitted during hazardous waste treating process (36). This study showed that emission of VOCs increased during mixing of hot asphalt with petroleum contaminated soil. For individual compounds, there were 100% to 800 % increases (Figure 7a. 7b); for total non-methane organic compound, increase was only 300% to 400% (Figure 8), therefore, the problem of increasing VOCs emission during processing can not be neglected.

According to EPA "Organic Air Emission Standard for Process Vents and Equipment Leaks in Hazardous Waste Treatment, Storage, and Disposal Facilities (TSDF)", The final rules for process vents require those owners or operators of TSDF subject to the provisions of new subpart AA: (1). reduce total organic emissions from all affected process vents at the facility to below 3 lb/h and 3.1 ton/yr. or (2). install and operate a control device that reduces total organic emissions from all affected process vents at the facility by 95 weight percent (37). It suggested increasing combustion temperature to totally destroy organic compounds or used other VOCs control equipment to meet this emission rate limit.

4.2. LEACHING TEST

4.2.1. Method detect limit and recovery

Method detect limit and range of recovery were shown in table 6.

Table 6. Detect limit and Recovery of Leaching Test

Compound	Method detect limit (ppb)	Range of recovery
Dichloromethane	0.29	82 +/- 32 %
1,2-Dichloroethane	0.47	76 +/- 21 %
1,1,1-Trichloroethane	0.39	73 +/- 28 %
Hexane	0.22	106 +/- 26 %
Benzene	0.26	88 +/- 16 %
Toluene	0.25	94 +/- 18 %
Tetrachloroethlene	0.13	108 +/- 24 %
Ethyl-benzene	0.28	79 +/- 17 %
p,m-Xylene	0.28	95 +/- 20 %
o-Xylene	0.24	91 +/- 21 %

4.2.2 Reproducibility test

The result of reproducibility was shown in table 7.

Table 7. Coefficient of Variation of Water Sample Analysis

Compound	C.V.	Concentration
Dichloromethane	12.6 %	12 ppb
1,2-Dichloroethane	24.8 %	26 ppb
1,1,1-Trichloroethane	21.4 %	8 ppb
Hexane	18.5 %	8 ppb
Benzene	14.3 %	14 ppb
Perchloroethylene	16.8 %	14 ppb
Ethyl-benzene	19.7 %	6 ppb
p,m-Xylene	9.6 %	5 ppb
o-Xylene	12.6 %	5 ppb

4.2.3 Leaching test of method I

The results of leaching test for method I were shown in table 8.

Table 8. Leachate Concentration of Method I

Compound	PCS#1	PCS#2	PCS#3	PCS#4	PCS#5	PCS#6
Dichloromethane	ND	ND	2.96	ND	ND	ND
1,2-Dichloroethane	ND	ND	0.88	0.16	0.18	1.51
1,1,1-TCE	ND	ND	8.01	ND	5.43	5.14
Hexane	0.23	ND	6.46	ND	2.43	0.85
Benzene	ND	ND	3.11	ND	2.19	ND
Toluene	ND	ND	ND	ND	ND	ND
Perchloroethlene	ND	ND	1.19	ND	0.97	ND
Ethyl-benzene	ND	ND	ND	ND	ND	ND
p,m-Xylene	ND	0.32	0.36	ND	0.33	1.69
o-Xlene	ND	ND	0.37	ND	ND	ND

4.2.4. Leaching test of method II

The results of leaching test for method II were shown in table 9.

Table 9. Leachate Concentration of Method II

Compound	PCS#1	PCS#2	PCS#3	PCS#4	PCS#5	PCS#6
Dichloromethane	ND	ND	2.34	ND	ND	ND
1,2-Dichloroethane	ND	1.79	1.18	1.95	ND	ND
1,1,1-TCE	13.99	14.24	25.84	21.75	26.08	26.45
Hexane	0.46	ND	6.24	ND	3.24	1.36
Benzene	8.04	4.46	4.36	7.20	8.37	4.35
Toluene	ND	ND	0.25	ND	ND	ND
Perchloroethlene	ND	ND	4.94	0.93	0.98	5.02
Ethyl-Benzene	ND	0.075	0.156	ND	0.056	0.055
p,m-Xylene	1.02	ND	1.62	1.66	1.09	1.65
o-Xylene	0.54	0.52	0.72	0.24	0.35	0.56

4.2.5. Long Term Leaching Test of PCS#3

The results of long term leaching test were shown in table 10.

Table 10. Leachate Concentration of PCS#3 Long Term Test

Compound	Method I			Method Two II		
	1 Day	7 days	30 days	1 day	7 days	30 days
Dichloromethane	1.82	2.33	3.12	ND	3.36	3.84
1,2-DCE	0.82	0.81	1.03	1.13	1.22	2.04
1,1,1-TCE	5.35	6.29	9.43	5.71	6.09	6.76
Hexane	6.01	6.32	6.87	5.78	6.03	7.13
Benzene	2.19	2.32	2.29	2.21	2.20	2.19
Toluene	ND	ND	ND	0.24	0.25	0.22
Perchloroethlene	1.01	1.11	1.12	0.96	0.97	1.02
Ethyl-Benzene	ND	ND	ND	0.046	0.052	0.12
p,m-Xylene	0.33	1.65	1.80	1.11	1.71	2.19
o-Xylene	0.26	0.28	0.30	0.65	0.71	0.68

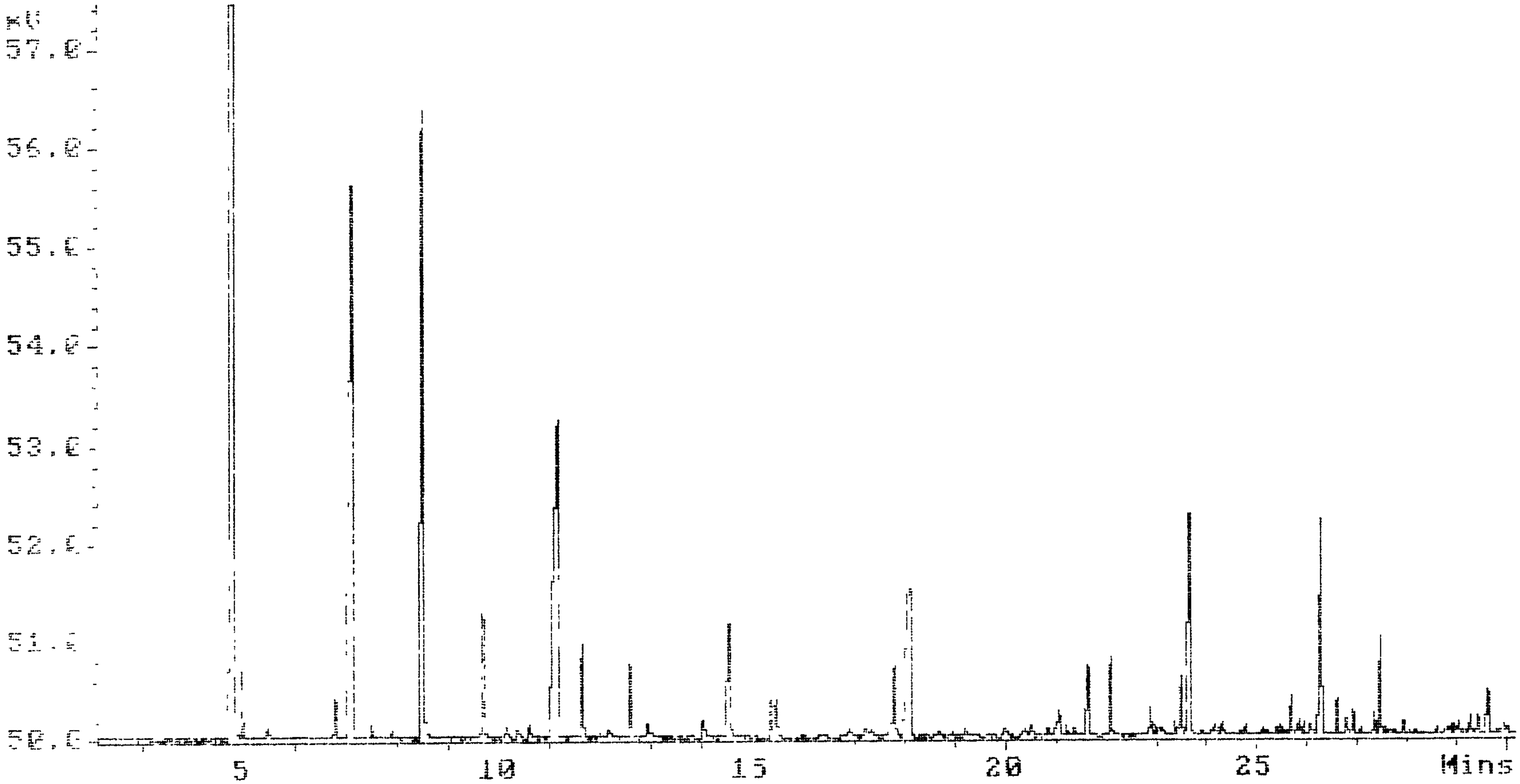


Figure 9. The Gas Chromatograph of Water Sample from Leaching Test

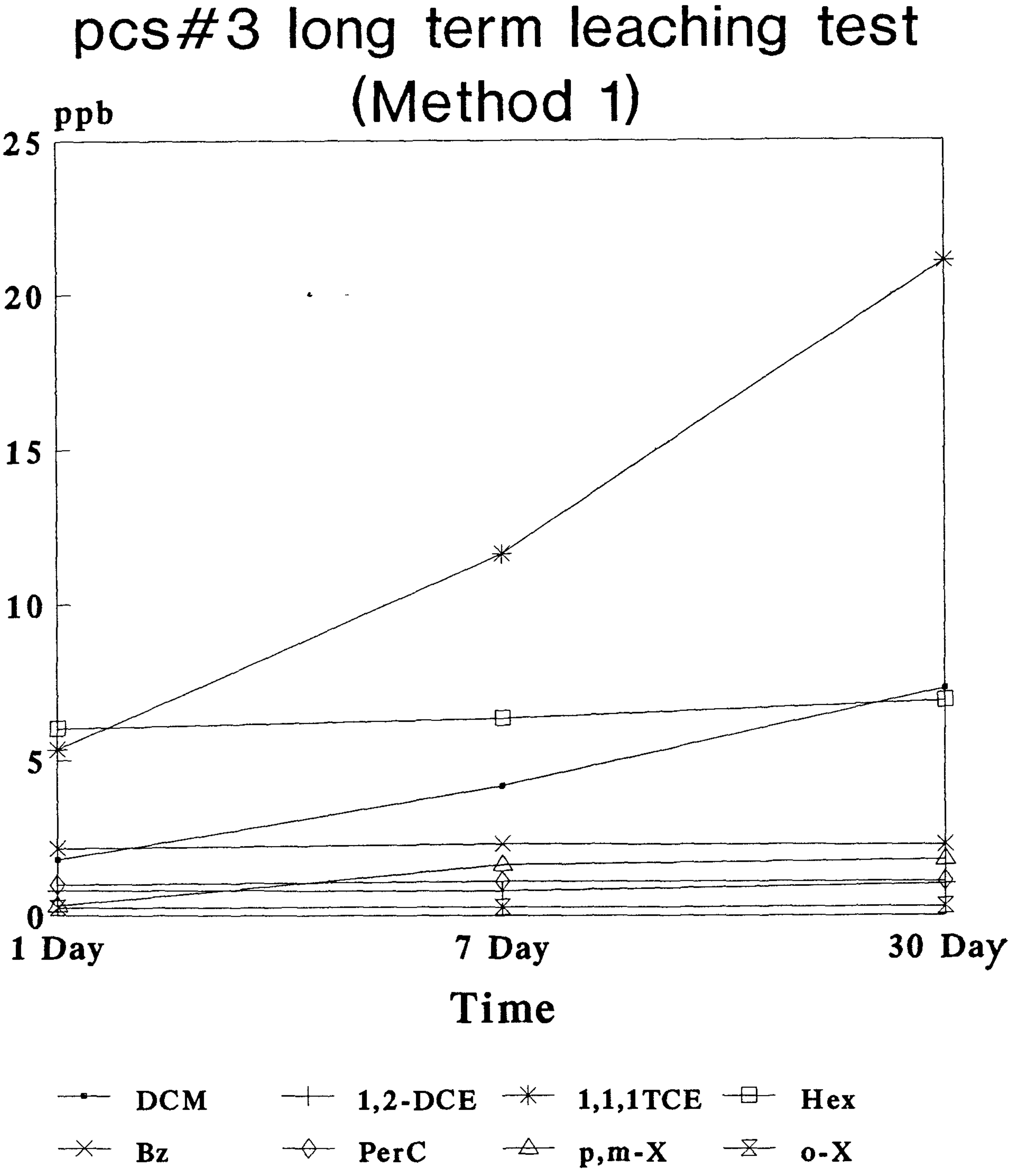


Figure 10. Diagram of Long Term Leaching Test by Method I

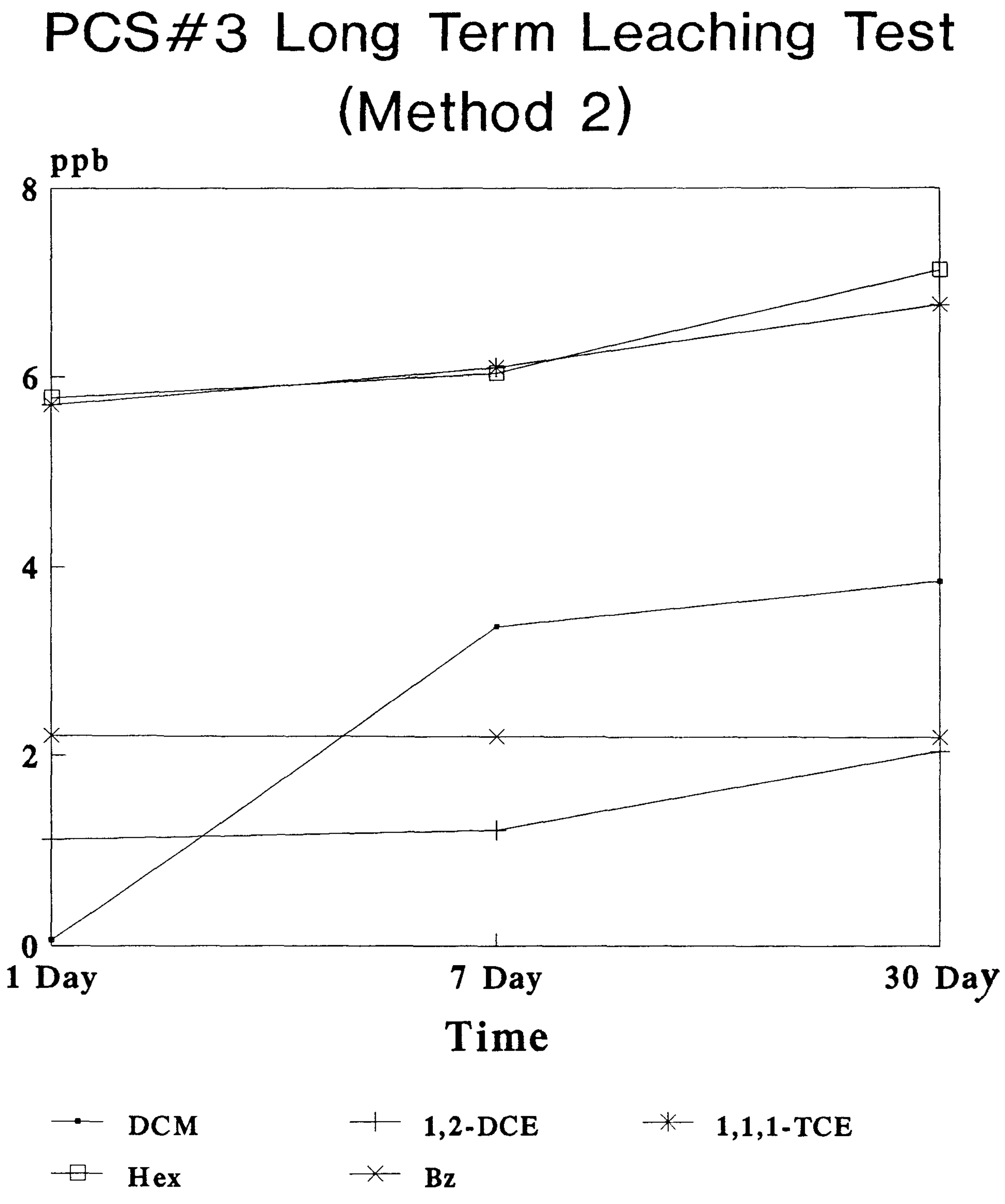


Figure 11a. Diagram of Long Term Leaching Test by Method II(1)

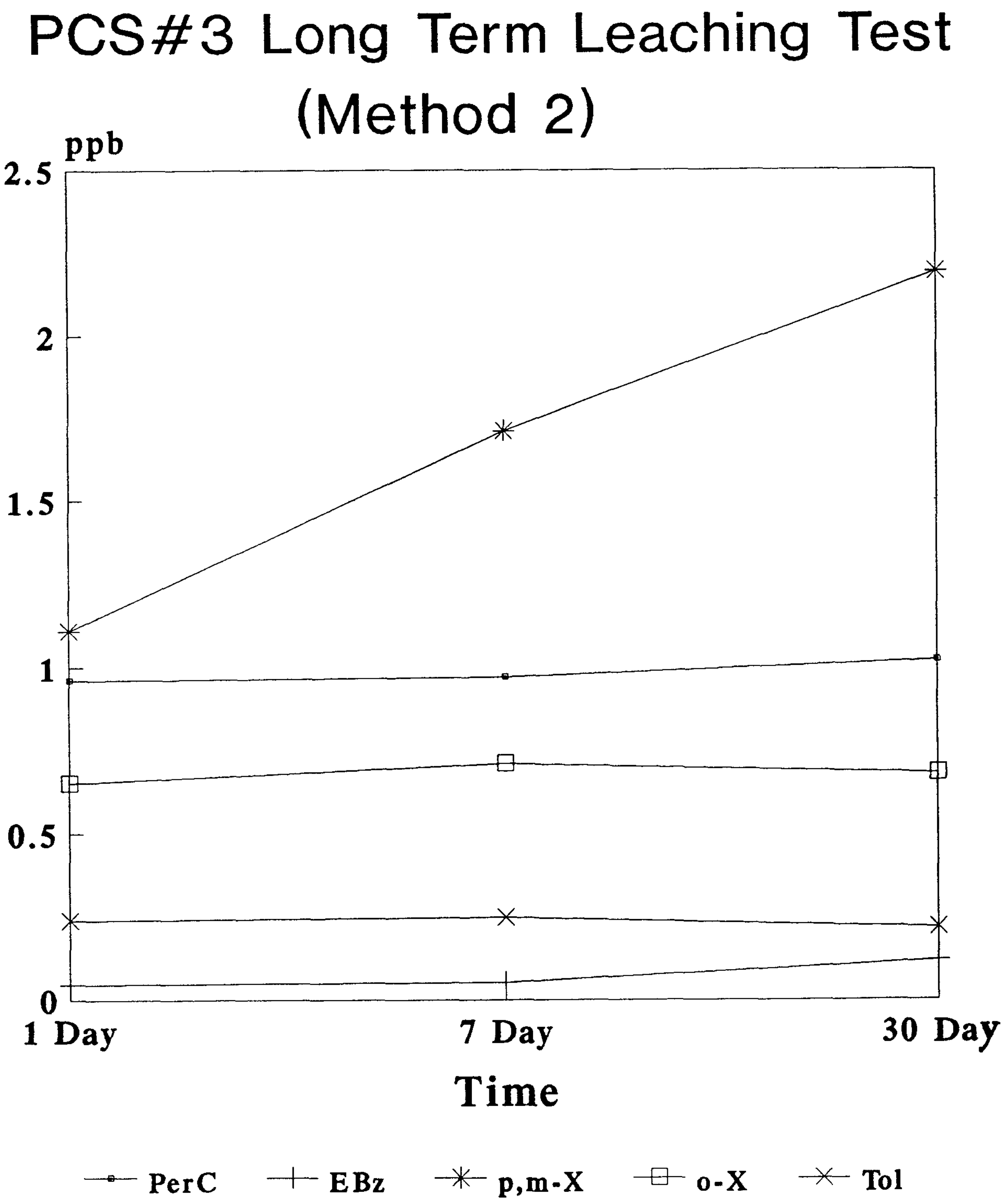


Figure 11b. Diagram of Long Term Leaching Test by Method II (2)

4.2.6 Discussion

4.2.6.1. Precision is a measure of agreement among individual measurement of the same property, under prescribed similar conditions. It may be expressed as the coefficient of variation. The coefficient of variation of multiple injection of standards was 9 to 25 % (Table 7.). Accuracy is a measure of the closeness of an individual measurement or the average of a number of measurements to the true value. It is usually expressed as a percent recovery. The range of recovery in the leaching test was between 60 % and 110 % (Table 6.), Therefore the results of this experiment are closed to reality.

4.2.6.2. Uniform leaching procedure was used to evaluate the potential leachability of asphalt mixture with contaminated soil. In method I, the contaminated soil was preheated at 130 °C for 5 hours, so a lot of VOCs were evaporated and few remained in the asphalt mixture (Table 8). In method II, some VOCs still retained in the asphalt mixture, but the concentration was also lower (Table 9, Figure 10, Figure 11a, 11b). The results were compared with EPA proposed regulatory limit (Table 11) for Toxicity Characteristic Leaching Procedure (TCLP) which was developed to evaluate leaching problem from solidified, immobilized waste materials. The compounds in our leaching test were much lower than that of the regulatory limits. If the asphalt mixture was used for paving, it would not cause severe problem of groundwater contamination.

4.2.6.3. When the Gas Chromatogrph for water sample was analyzed, it was found that there was very few heavier hydrocarbon compounds in the leaching medium. It seems to that the heavier hydrocarbon compounds were either incinerated or solidified in the asphalt matrix, therefore, production of HMA with PCSs is environmental suitable method to remediate contaminated soils with heavier petroleum hydrocarbons. Control of emission of VOCs is an important issue in implementing this technique.

Table 11. EPA Proposed Regulatory Limits For TCLP Extracts

EPA HW Number	Constituents	CAS number	Regulatory Level(ppm)
D019	Benzene	71-43-2	0.07
D025	Chloroform	67-66-3	0.07
D031	1,2-Dichloroethane	107-08-2	0.40
D032	1,1-Dichloroethylene	75-35-4	0.1
D047	Perchloroethylene	127-18-4	0.1
D049	Toluene	106-88-3	14.4
D050	1,1,1-Trichloroethane	71-55-6	30.0
D052	Trichloroethylene	79-01-6	0.07
D066	Vinyl Chloride	75-01-4	0.05

Chapter 5
CONCLUSION

The concentration of 11 volatile organic compounds (VOCs) and total non-methane organic compound (NMOC) were measured by solid adsorbent sampling and thermal desorption, followed by gas chromatographic analysis. The result showed that VOCs emission increased during mixing of hot asphalt with petroleum contaminated soil. The emission factor is 0.065 pounds carbon per ton products of asphalt concrete. Individual compounds increased at different rates. It is suggested to use another VOCs pollution control device to reduce VOCs emission.

A uniform leachability test was designed to evaluate VOCs leaching from the mixture of asphalt and petroleum contaminated soil. The leachate concentration in the leaching media was much lower than that of EPA Proposed Regulatory Limits for Toxicity Characteristic Leaching procedure. It suggested either low concentration of VOCs in the asphalt mixture or no significant leaching of VOCs from the asphalt into leaching medium.

It may be concluded that the incorporation of asphalt with PCSs for road paving is an environmental safe method of recycling contaminated soils, if there further reduction of air VOCs emission. Further reduction of VOCs can be achieved by increasing the temperature of incinerator or by application other VOCs control devices.

BIBLIOGRAPHY

1. Fairweather, V. "U.S. Trackles Leaking Tanks." *Civil Engineering.* 60 (1990): 46.
2. Mclean, M. E. "Remedial Options for Leaking Underground Storage Tanks." *Journal of the Air Pollution Control Association.* 38 (1988): 428.
3. Office of Emergency Remedial Response. U.S.EPA. "Conducting Remedial Investigations/Feasibility Studies for CERCLA Municipal Landfill Sites." *EPA/540/P-91/001* (1991): 56.
4. Gibbons, J. J. & R. Soundararajan. "The Nature of Chemical Bonding Between Modified Clay Minerals and Organic Waste Materials." *American Laboratory.* July (1988): 38.
5. Donnachie, R. "On-Site vs Off-Site Treatment." *Pollution Engineering.* 23 (1991): 62.
6. Fitzpatrick, V.F., C.L. Timmerman, & J.L.Buelt. "In Situ Vitrification - An Innovative Thermal Treatment Technology." *Second International Conference on New Frontiers for Hazardous Waste Engineering.* Research Laboratory. Cincinnati. OH. EPA/600/9-87/018F. (1987): 305-322.
7. Iskandar, I. K., & T. F. Jenkins. "Potential Use of Artificial Ground Freezing for Contaminant Immobilization." *International Conference on New Frontiers for Hazardous Wastes Management.* U.S. EPA, Hazardous Wastes Engineering Research Laboratory. Cincinnati. OH. (1985): 128-137.
8. U.S. EPA. "Handbook: Remedial Action of Waste Disposal Sites (Revised)." EPA*/625/6-85-006.* (1985): 84-86.
9. Glynn, W., & M. Duchesneau. "Assessment of Vacuum Extraction Technology Application: Belleview, Florida LUST Site." *Prepared under Contract No. 68-03-3409 for U.S. EPA.* Risk Reduction Engineering Laboratory. Cincinnati. OH. (1988).
10. Nash, J. H. "Project Summary: Field Studies on in Situ Soil Washing." EPA Hazardous Waste Engineering Research Laboratory. Cincinnati. OH. *EPA/600/S2-87/110* (1988).
11. Nakayama, S.," Ozone." *Science and Engineering.* 1 (1979): 119-132.
12. Min, M., R. Barchour., & J. Hwang. "Treating Land Ban Waste." *Pollution Engineering.* August (1991): 70.

13. Dev, H., G. C. Sresty., & D. Downey. "Field Test of the Radio Frequency in Situ Soil Decontamination Process. in: Superfund'88." *Proceedings of the 9th National Conference*. The Hazardous Materials Control Research Institute, Silver Spring, MD, (1988).

14. Bossert, R., & D.Bartha. "The Fate of Petroleum in Soil Ecosystems." *Petroleum Microbiology*. R.M. Alas, Ed., Macmillian Co., New York, (1984): 435-473.

15. Arniella, E. F., & R.E.Holley. "Cleaning up Soils Contaminated with Petroleum Hydrocarbon." *Water Environment and Technology*. 3 (1991): 22.

16. Thomas, W.B. "Emission of Volatile Organic Compounds from Drum Mix asphalt plants." U.S. EPA, Washington. DC. *EPA/600/2-81-026*. (1981).

17. Edwin, F.B. "An Overview of the History, Present Status, and Future Direction of Solidification/Stabilization Technologies for Hazardous Waste Treatment." *Journal of Hazardous Materials*. 24 (1990):103-109.

18. Conner, J. "Chemical Fixation and solidification of hazardous Waste." Van Nostrand Reinhold, Princeton. N.J. (1990): 89.

19. Prendergast, J. "Anatomy of Asphalt." *Civil Engineering*. 61 (1991): 56.

20. Hubbard, J., S. Tsadwa., N. Willis., & M. Evans. "Site Sampling and Treatability Studies for Demonstration of WasteChem's Asphalt Encapsulation Technology Under EPA's SITE Program." *Journal of Air & waste Management Association*, 40 (1990): 1436.

21. Kostecki, P.T., E. J. Calabrese., & E. J. Fleischer. "Asphalt Batching of Petroleum Contaminated Soils as a Viable Remedial Option", *Petroleum Contaminated Soils,Vol (I)*, P. T. Kostecki & E. J. Calabrese, Ed., Lewis Publishers, Inc., (1988): 177.

22. Czarnecki, R.C. "Making Use of Contaminated Soil." *Civil Engineering*. december (1988): 72.

23. Eklund, K. "Incorporation of Contaminated Soils into Bituminous Concrete." *Petroleum Contaminated Soils, Vol.(I)*, P.T. Kostecki & E. J. Calabrese, Ed., Lewis Publishers, Inc., (1988): 191.

24. Atmospheric Research and Exposure Assessment Laboratory, U.S. EPA, "Method TO1" *Method for the Determination of Volatile Organic Compounds in Ambient Air Using Tenax Adsorption and Gas Chromatography/Mass Spectrometry*. Research Triangle Park. NC. EPA/600/4-89/017, (1988): 67.

25. Office of Air Quality Planning and Standards, U.S.EPA, Compilation of Air

Pollutant Emission Factors. *Vol.I: Stationary Point and Area Sources.* Research Triangle Park. NC. (1985): 81.

26. Municipal Environmental Research Laboratory, U.S. EPA. "Guide to The Disposal of Chemically Stabilized and Solidified Waste." *SW-872.* Cincinnati. Ohio. (1982): 88-108.

27. U.S. EPA, "Toxicity Characteristic Leaching Procedure (TCLP) (Method 1311)." *Federal Register. Vol.55, No.61, 29 March* (1990): 11813-11863.

28. Ham, R., M. A. Anderson., R. Stegmann., & R. Stanforth. "Background Study on The Development of a Standard Leaching Test." *EPA-600/2-79-109,* U.S.EPA. Cincinnati. Ohio. (1979): 33-41.

29. Flotard, R. D., M. T. Homsher., J. S. Wolff., & J. M. Moor. "Volatile Organic Analytical Methods Performance and Control Consideration." *Quality Control in Remedial Site Investigation: Hazardous and Industrial Solid waste Testing, Fifth Volume, ASTM STP 925,* C.L. Perket, Ed., American Sociaty for Testing and Materials. Philadelphia. (1986): 89.

30. Van der Sloot, H. A. "Leaching Behavior of Waste and Stabilized Waste Materials; Characterization for Environmental Assessment Purposes." *Waste Management & Research.* 8 (1990): 215.

31. ACS Committee on Environmental Improvement. "Guidelines for Data Acquisition and Data Quality Evaluation in Environmental Chemistry." *Analytical Chemistry.* 52 (1980): 2242-2249.

32. Lianyi Z. "Preconcentration and Direct Flame Ionization Method for Measurement of Non-Methane Organic Compounds in Ambient Air and Statistical Analysis of Experimental Data." *MS Thesis.* NJIT. (1988).

33. De-rong L. H. "Stability of Hot Mix Asphalt with Petroleum Contaminated Soils" MS Thesis. NJIT. (1991).

34. U.S. EPA. "Appendix A to Part 136 - Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater." *Federal Register. Vol.49, No.209. October 26.* (1984).

35. Dupont, R. R. "Measurement of Volatile Hazardous Organic Emissions from Land Treatment Facilities." *Journal of the Air Pollution Control Association.* 37 (1987): 174.

36. Shen, T. T., T. P.Nelson,. & C. E. Schmidt. "Assessment and control of VOC emissions from waste disposal." *Critical Reviews in Environmental Control.* 20 (1990): 43.

37. U.S. EPA, Hazardous Waste Treatment, Storage, and Disposal Facility - Organic Air Emission Standards for Process Vents and Equipment Leaks. *Federal Register, Vol.55, No.120/ Thursday. 21* (1990).