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Oil, grease and used petroleum oil management and environmental economic issues

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Materials

ABSTRACT

Purpose: This paper undertakes to answer the question of how used petroleum oil and grease enter groundwater or to the drain becoming both environmental and economic problems to utility companies.

Design/methodology/approach: Laboratory methodology was based on modern instrumentation validated further with experimental investigation. Petroleum-contaminated soil samples were analyzed for oil and grease (O/G) content, total petroleum hydrocarbons (TPH), and volatile aromatic compounds: benzene, toluene, ethylbenzene, and xylenes (BTEX) and naphthalene. Gas chromatography-Mass Spectrometry (GC/MS) was used to analyse BTEX and naphthalene analytes.

Findings: The results show that total petroleum hydrocarbon fraction (TPH) accounted for oil and grease (O/G) and the ratio of [TPH]/[O/G] ranged from 12% to 50%. The results of volatile organic fraction (BTEX) accounted for only a small part of total TPH and the ratio of [BTEX]/[TPH] ranged below 1%. The concentration of four samples for TPH test exceeded the regulatory limit of 500 ppm for hydrocarbons. The gas chromatography-flame ionization detector (GC-FID) method appear to offer the best basis for standard TPH test in soil and groundwater verification of site cleanup.

Research limitations/implications: In the future it will be possible to apply the procedures to other more complicated cases e.g. used oil containing more than 1000 ppm total halogens, which is regulated as hazardous waste. **Practical implications:** Promising directions for adaptation of appropriate pre-treatment standard processes for recycling programs, pollution prevention and reduction of maintenance cost.

Originality/value: The gas chromatography-flame ionization detector (GC-FID) methods appear to offer the best hope for standard TPH test in soil and groundwater verification of site cleanup. Implementation of management standards and a permit policy for O/G and used oil generators will be issued to each facility. **Keywords:** Amorphous materials: Physical properties: Handling and disposal; Oil and grease: Used oils

1. Introduction

Fats, oil and grease, also called FOG in the wastewater business can have negative impacts on wastewater treatment systems. Blockages in the wastewater collection system are serious, causing sewage spills, manhole overflows, or sewage backups in homes and businesses. Cities spend billions of dollars every year unplugging or replacing grease-blocked pipes, repairing pump stations, and cleaning up costly and illegal wastewater spills. These repairs cost money and may lead to higher local wastewater rates, thereby affecting the company's

profit margin. There is a combination of four forms in which oil and grease can exist namely, oil dissolved in water, chemically emulsified oil, free oil which is a liquid that floats to the surface of water, and mechanically emulsified oil.

Federal pretreatment regulations (40 CFR 403.5(b)(6)) specifically prohibit petroleum oil, non-biodegradable cutting oil, or products of mineral oil origin in amounts that will cause interference or pass through. However, the federal regulations are silent on other types of oils and greases and most cities have regulations that specify limits and enforcement of oil and grease (lipids) discharges from restaurants [1]. When setting FOG limits, municipalities must take into consideration many things such as the protection of the collection system and wastewater treatment plants (WWTP), the practicality of monitoring and enforcing limits, cost and manpower needed for monitoring.

Numerical Limits vs. best management practices

In 1949, the Federation of Sewage Works Associations (now known as the Water Environment Federation, WEF) published a Manual of Practice (MOP) in which it recommended 100 mg/L as a maximum limit of oil and grease. However, the MOP did not specify the importance of the origin of the FOG, which could be either petroleum or animal and vegetable. WEF's MOP3 (1973) cited levels of FOG in domestic wastewaters to be in the range of [mg/L] 16 to 105 [2]. They further recommended limits on petroleum-based oil at 25 mg/L, though 40 CFR 419 (petroleum refining category) limits indirect discharges at 100 mg/L. The specific federal pretreatment regulations, 40 CFR 403.5(b)(6), prohibit "petroleum oil, non-biodegradable cutting oil, or products of mineral oil origin in amounts that will cause interference or pass through." Some municipalities specify different limits for FOG with different origins, such as 100 mg/L for petroleumbased (or mineral) FOG and 300 mg/L for animal and vegetablebased FOG. In most municipalities, FOG limits of [mg/L] 100 to 300 are protective of the collection system, but a limit that works in one situation may not work in another. Limits may need to vary depending on different factors, such as the number of wet wells, type of sewers, slope of sewers, flow in sewers, and history of grease related clogs [2].

In 1975, EPA concluded that animal and vegetable FOG can be metabolized by microorganisms during biological treatment and may be removed by up to between 80% and 90%. Oily material is adsorbed by the floc at a wastewater treatment plant and is slowly metabolized. This can often produce a less dense floc, which can be easily washed out of a clarifier. EPA went on to suggest that influent to biological treatment should ideally contain less than 50 mg/L of FOG and that dilution in the collection system would reduce any 100 mg/L discharges to acceptable levels for treatment at the plant, assuming the FOG gets to the plant. Preventing FOG buildup in the collection system is the goal of FOG control measures. Many cities have found that requiring restaurants to implement best management practices (BMP) is an effective tool in controlling FOG without requiring extensive monitoring. BMPs can range from posting "no grease" signs above sinks and on the front of dishwashers to requiring grease traps and undersink grease interceptors to be routinely cleaned on a set time schedule and/or when a certain volume is reached. Grease interceptors, grease traps, and oil/water separators are a devices designed to remove O/G and petroleum-based oil from the waste stream. Grease

intercept are not required for private residences or dwellings. Automotive-related facilities, which may contribute petroleum-based oil to the collection system shall be required to install oil/water separator [2].

Cleanup of soil contaminated with used oil

Used oil is any oil that has been refined from crude oil or any synthetic oil made from coal, shale or polymer-based starting material. As the name implies, it must have been used, and as a result of such use, it is contaminated with physical impurities (like metal fines, sawdust or dirt) or chemical impurities (like fuel, solvents, halogens or water). Common uses include lubricants and heat transfer fluids. Used oil does include: engine oil, transmission fluid, compressor oil, metalworking oils, hydraulic oil refrigeration oil, and electrical insulating oil. Used oil does not include: vegetable oil or animal oil, even when used as a lubricant, virgin (unused) oil, bottom clean-out waste from virgin oil storage tanks, petroleum-derived products like antifreeze or kerosene, and petroleum-distillates used as solvents [3]. The contaminated soil samples should be collected from the areas where the highest levels of contamination are most likely to exist. The subsurface soil risk based on screening laboratory analysis levels of 0.26 mg/kg benzene, 200 mg/kg ethylbenzene, 170 mg/kg toluene and 1900 mg/kg total xylenes, and total petroleum hydrocarbons (TPH) in the oil and grease range less than or equal to 500 mg/kg. If initial laboratory analyses indicate that soil within the contaminated area is below the subsurface soil risk based screening levels for benzene, toluene, ethylbenzene and xylenes (BTEX), and total petroleum hydrocarbons is less than 500 mg/kg, we may request that the contaminated soil be left in place for natural biodegradation to occur [3]. Confirmatory samples should be analyzed for total petroleum hydrocarbons (TPH) in the oil and grease range, BTEX and any other constituents reasonably expected to be present based on knowledge of the origin of the used oil and initial sample results [4].

Petroleum hydrocarbons (PHCs) are common site contaminants, but they are not generally regulated as hazardous wastes [5]. With the exception of the BTEX compounds, the US EPA regulates only sixteen compounds out of the thousands found in petroleum [6]. Total petroleum hydrocarbons (TPH) is a term used to describe a broad family of chemical compounds that of water, soil, or air as a general indicator of petroleum content [7].

Petroleum hydrocarbons released to the soil may move through the soil to the groundwater. Individual contaminant compounds at the site may separate from the original mixture, depending on the chemical properties of the compounds. Some of these compounds will evaporate into the air and others will dissolve into groundwater and move away from the release area. Some compounds will attach to particles in the soil and may remain in the soil in the groundwater. Individual contaminant compounds the soil for the long time, while others will be broken down by organisms found in the soil. It is useful to measure the total amount of all hydrocarbons found together in particular samples; individual hydrocarbons present in petroleum products are as follows: gasoline $(C_6 - C_{12})$, diesel $(C_8 - C_{26})$, kerosene $(C_8 - C_{18})$, fuel oil $(C_{17} - C_{26})$, and lubricating oils $(C_{15} - C_{50})$ [8,9].

Used oil is significantly contaminated with aliphatic and polyaromatic hydrocarbons (PAHs). The content of aliphatic and aromatic hydrocarbons measured in used engine oil was (in ppm)

as follows: trichlorotrifuoroethane (160), 1,1,1-trichloroethane (200), trichloroethylene (100), tetrachloroethylene (106), benzene (20), toluene (380), xylene (530), benz(α)antracene (12), benzo(α)pyrene (10), naphthalene (330), and polychlorinated biphenyl, PCBs (5) [8,10].

Table 1. Solubility of BTEX compounds (benzene, toluene, ethylbenzene and (o-, m-, p-) xylene in water [5]

Product	Benzene [ppm]	Toluene [ppm]	Ethylben- zene [ppm]	Xylenes [ppm]	
Gasoline Diesel fuel Fuel oil # 6	29.5 0.13 0.01	42.6 0.41 0.03	2.4 0.18 0.007	14 0.70 0.05	
Drinking water (MCL) ^a	0.005	2.0	0.66	0.44	

^aMaximum contamination level in drinking water

Unleaded gasoline is rich in volatile hydrocarbons with concentration above 10,000 ppm (benzene 13800, toluene 58000, ethylbenzene 12500, o- and p-xylene, 33100, and m-xylene 32100). Diesel fuel has volatile aromatic concentrations about two orders of magnitude lower than gasoline (benzene < 125, toluene 359, ethylbenzene 312, m-xylene 669 and o- and p-xylenes 638) [11].

2. Testing methods

2.1. Oil and grease

"Oil and grease (O/G)" is defined as any material recovered as a substance in the form of an organic solvent from soil sample. Oil and grease is composed primarily of a fatty matter from animal and vegetable sources, hydrocarbons of petroleum origin, the interferences include sulfur compounds, certain organic dyes, and chlorophyll [6,12]. Many solvents are used in analytical methods of O/G: petroleum ether, trichlorotrifluoroethane, a mixture of 80% n-hexane + 20% methyl-*tert*-butyl ether, and currently n-hexane [12].

If O/G is present in excessive amounts, it may interfere with aerobic and anaerobic biological process and may lead to decreased wastewater treatment efficiency. Knowledge of the quantity of O/G present is helpful in proper design and operation of wastewater systems and also for identifying treatment difficulties.

2.2.TPH analysis overview

The TPH value represents a mixture of compounds and can be measured by one of several analytical methods, some of which have been used for decades and others developed in the past several years [5].

Commonly used method in last decade was EPA method 418.1, which measures total hydrocarbons but does not provide information on the composition (individual constituents of the hydrocarbon mixture) [9]. The amount of TPH measured by this method depends on the ability of the solvent to extract hydrocarbons from the environmental media and on the absorption of infrared (IR) light by the hydrocarbons in the solvent extract. Negative bias may also be introduced *via* poor extraction efficiency of Freon-113 for high-molecular-weight hydrocarbons, differences in molar absorption, and removal of five-to six-ring alkylated aromatics during the silica gel cleanup procedure [9]. While interpreting results, it should be remembered that method 418.1 can also indicate compounds other than petroleum hydrocarbons (e.g., humic acid).

Most reliable analytical method commonly used for TPH is a modified EPA method 8015B [13]. This method reports the concentration of purgeable fractions as gasoline range organic (GRO) hydrocarbons measured by purge-and-trap gas chromatography (GC-FID) analysis using a flame ionization detector (FID). The semivolatile fractions as diesel range organic (DRO) hydrocarbons are extracted prior to analysis by GC-FID. The results are reported most frequently as single numbers (GRO+DRO) for purgeable and extractable hydrocarbons. In gasoline, hydrocarbons correspond to C_6 - $C_{10\text{-}12}$ petroleum fraction and in diesel hydrocarbons correspond to $C_{8\text{-}12}$ - $C_{24\text{-}26}$ petroleum fraction.

Currently, many laboratories have adapted a new EPA method 1664: "N-hexane extractable material (HEM) and silica gel treated n-hexane extractable material (SGT-HEM) by extraction and gravimetry (oil and grease and total petroleum hydrocarbons" [14]. This method uses sonication technique in analysis of soils and sediments for determination of O/G and TPH and replaces EPA method 418.1.

2.3. Volatile aromatic fraction

TPH compounds are relatively insoluble in water, with only BTEX compounds (benzene, toluene, ethylbenzene, xylenes), naphthalene and certain short-chain aliphatic hydrocarbons showing some appreciable potential for water solubility. The information presented in table 1 show why much attention is often focused on sites contaminated by gasoline. Gasoline mixtures have much higher percentage of light fraction aromatic hydrocarbons, such as the BTEX aromatics, than other bulk fuel products. This can lead to much higher level of contamination in groundwater from gasoline than from petroleum mixtures with less soluble components.

Soil contamination has been a growing concern because it can be a source of groundwater (drinking water) contamination, and watered petroleum residuals may stay bound to soil for years. The focus of this study was to determine the organic contaminant content in soil samples. Oil and grease content were measured using EPA method 9071A [15], total petroleum hydrocarbons (TPH) using EPA method 8015B (gas chromatography-flame ionization detector) [13], volatile fraction of aromatic hydrocarbons BTEX (benzene, toluene, ethylbenzene, xylenes) and naphthalene using EPA method 8020B [16].

Table 2. Oil/grease (O/G), total petroleum hydrocarbons (TPH) and volatile aromatic compounds (BTEX) in soil samples

Sample O/G		TPH [TPH]/[O/G] (BTEX) ^a Volatile aromatic compound		• • • • • • • • • • • • • • • • • • • •	[BTEX	
	(ppm)	(ppm)	(%)	(ppm)	[TPH]	[O/G]
EF	A 9071A	EPA 8015B	I	EPA 8020B (*)	%) (%)
1	(70	200	41.0	D (0.60) + 1 (0.20) 1 (0.12)	0.27	0.16
1	670	280	41.8	Benzene (0.60), toluene (0.30), xylene (0.13)	0.37	0.16
2	8200	950 ^b	11.6	Benzene (0.40), ethylbenzene (0.05),	0.37	0.04
		440		(2.75), xylene (0.30)	^ ^ ^	0.02
3	720	110	15.3	Toluene (0.10), ethylbenzene (0.04),	0.22	0.03
				xylene (0.10)		
4	570	320	45.7	Benzene (0.65), ethylbenzene (0.10),	0.35	0.16
				xylene (0.35)		
5	1240	420	33.9	Benzene (0.90), ethylbenzene (0.20),	0.36	0.12
				xylene (0.40)		
6	710	280	39.4	Benzene (0.90), naphthalene (0.20),	0.54	0.21
				xylene (0.40)		
7	1400	620 ^b	44.3	Benzene (0.50), ethylbenzene (0.20),	0.40	0.18
			toluene	(1.50), xylene (0.30)		
8	2100	470	22.4	Ethylbenzene (0.20), naphthalene (0.10),	0.19	0.04
				xylene (0.60)		
9	820	320	39.0	Benzene (0.70), ethylbenzene (0.20),	0.38	0.15
				xylene (0.32)		
10	1710	410	24.0	Benzene (0.90), toluene (0.60), xylene (0.30)	0.38	0.09
11	370	140	37.8	Benzene (0.20), toluene (0.50), xylene (0.20)	0.64	0.24
12	320	160	50.0	Benzene (0.20), toluene (0.40), xylene (0.10)	0.44	0.22
13	2700	370	13.7	Benzene (0.20), toluene (0.20), xylene (0.12)	0.14	0.02
14	620	180	29.0	Benzene (0.25), ethylbenzene (0.10),	0.25	0.07
			1	coluene (0.40)		
15	1300	520 ^b	40.0	Benzene (2.00), ethylbenzene (0.10),	0.60	0.24
				xylene (1.00)		
16	1500	510 ^b	34.0	Toluene (2.20), ethylbenzene (0.10),	0.39	0.13
				xylene (0.70)		
17	1200	340	28.3	Benzene (0.30), toluene (0.60), xylene (0.20)	0.32	0.09
-				(*****)		

Quality control (QC) parameters: Reference standard material, SRM (85% – 115% recovery), Continuing check standard, CSTD (80% – 120%), Lab spike blank, LSB (85% – 115%), Lab spike blank duplicate, LSBD (85% – 115%), Lab spike matrix, LSM (80% – 120%), Lab spike matrix duplicate LSMD (80% – 120%).

^aAccuracy and precision of O/G, TPH and BTEX analysis: Accuracy was determined as a ratio of LSB _{found} and LSB _{true} (85% to 115%), or LSM _{found} and LSM _{true} (80% to 120%); the precision was determined by calculating the difference between the results found for the LSB and LSBD, and then dividing the difference by the average of the two results (4% to 7%).

Gas chromatography-mass spectrometry (GC/MS) was employed for analysis of volatile aromatic fraction of hydrocarbons. Results for volatile aromatic fraction of hydrocarbons (BTEX) and for total petroleum hydrocarbons (TPH) have been compared (Table 2).

2.4. Experimental

Samples were obtained at two different locations at a rerefinery facility site at 10 cm deep. Soil samples were extracted using procedures of EPA methods 9071A, 8015B and 8020B. Oil/grease method 9071A is a procedure for extracting nonvolatile and semivolatile organic compounds from soil samples (see Table 2) [15]. The sonication process ensures close contact of the matrix with hexane during the extraction. The method is not applicable to measurement of light hydrocarbons that volatilize at temperature below 70 °C with method reported limit of 50 ppm. Total petroleum hydrocarbons were measured by gas chromatography-flame ionization detector (GC/FID) according to method 8015B; with method reported limit of 10 ppm for soil (see Table 2) [13].

The gas chromatography-mass spectrometry (GC/MS) was used for the analysis of benzene, toluene, ethylbenzene, xylene, and naphthalene in soil samples. The method reported limit was 0.025 ppm for benzene, toluene, ethylbenzene, m-xylene and 0.050 ppm for o- and p-xylene and naphthalene. The standards were prepared as specified in EPA method 8020B (see table 2) [16].

2.5. Quality assurance (QA)/quality control (QC)

To assure the accuracy and precision of a measurement method, a series of QA/QC procedures were used to validate the data from EPA methods (see summary table 2). During extractions, blank extraction

Table 3.

Leaching test (TCLP) efficiency for BTEX compounds in unleaded gasoline and diesel fuel contaminated river and topsoil [11], used oil and sludge sample (from this work)

BTEX - Compound -	Gasoline nominal concentration			Diesel nominal concentration			Used oil	Sludge		
	1000 ppm		10000ppm		1000 ppm		10000 ppm		sample	sample
	TCLP (ppm)		TCLP (ppm)		TCLP (ppm)		TCPL (ppm)		TCLP(ppm)	TCLP(ppm)
	Rivera	Top ^a	River	Top	River	Тор	River	Тор	used oil	sludge
	soil	soil	soil	soil	soil	soil	soil	soil	sample	sample
Benzene	0.24	$<$ MDL b	2.38^{d}	0.11	0.052	ND^{c}	0.043	0.004	< 0.025	< 0.025
Toluene	1.48	0.008	13.1	2.62	0.052	<mdl< td=""><td>0.006</td><td>0.006</td><td>0.030</td><td>0.030</td></mdl<>	0.006	0.006	0.030	0.030
Ethylbenzene	0.33	0.006	2.53	1.21	0.015	<mdl< td=""><td>0.047</td><td>0.052</td><td>< 0.025</td><td>< 0.025</td></mdl<>	0.047	0.052	< 0.025	< 0.025
m-Xylene	0.88	0.022	6.56	3.46	0.033	0.004	0.099	0.106	< 0.025	< 0.025
o- and p-	0.90	0.029	6.72	3.67	0.034	0.004	0.104	0.110	< 0.05	< 0.05
Xylenes		0.029	0.72	3.07	0.034	0.004	0.104	0.110	< 0.03	<u> </u>

^cND = analyte not detected,

samples, duplicate samples, and standard reference materials (SRM) were processed along with the samples.

Blank extraction samples were run to detect contamination introduced in the sample processing and analysis procedure. Clean sand with surrogate recovery standards was used for the extraction blanks. Additionally, sample duplicates were also extracted to assure reproducibility of the method. The concentrations reported did not deviate more than 20% between the duplicates and reference materials. An extraction blank was processed and analyzed with each extraction sample set (10 samples). In addition, laboratory spike blank (LSB) and laboratory spike blank duplicate (LSBD) were analyzed with each extraction sample set (10 samples). The reported values LSB and LSBD could not deviate more than 15% from the certified values. The method detection limits were determined using EPA protocol [17] and method reported limits (MRLs) values are given in section 2.4.

3. Results and discussion

3.1. Oil and grease (O/G) and total petroleum hydrocarbons (TPH)

The results of the oil/grease (O/G), total petroleum hydrocarbons (TPH), for petroleum contaminated soil samples are presented in Table 2. The difference of the [O/G] – [TPH]) represents the polar fraction. Comparison of the initial O/G and TPH values ([O/G] – [TPH])/[O/G]) shows that polar fraction consists of 50% to 86%. The results shown in table 2 indicate that total petroleum hydrocarbon fraction (TPH) accounted for O/G and the [TPH]/[O/G] ratio ranged from 12% to 50%.

The results based on the 418.1 and 8015B methods, obtained from 155 laboratories participating in three proficiency-testing rounds, were evaluated [18]. Participants were supplied with soil samples with different levels of mineral oil content. These two methods (418.1 and 8015B) were compared using 1,1,2-trichlorotrifluoroethane (with IR quantification) and hexane (with GC/FID quantification) as the extraction solvents. The consensus

means obtained with (GC-FID) were typically 10% to 20% higher than those found with IR-spectroscopy.

EPA method 418.1 based on the IR absorption specified in the methodology strongly favors detection of aliphatic over aromatic hydrocarbons, so is unsuitable for the quantification of TPH contamination which is mainly attributable to aromatics. Also, the method has no opportunity to assess the type of hydrocarbon contamination present [19]. Analysis of the extract by GC-FID yields a total recoverable hydrocarbon result that is fundamentally different to that which was obtained by IR.

3.2. Volatile organic compounds

Currently, the most sophisticated method of petroleum analysis is GC-MS, which provides detailed information on specific hydrocarbon compounds in petroleum. The results shown in Table 2 indicate that volatile organic fraction (BTEX) accounted for only a small part of total TPH of the contaminated samples and the ratios of [BTEX]/[TPH] ranged from 0.14% to 0.64%. The ratios of [BTEX]/[O-G] ranged from 0.02% to 0.24%.

A good correlation between measured BTEX and TPH was obtained (Fig. 1). This yielded the relation: BTEX (ppm) = 0.004 TPH (ppm) + 0.0034; $R^2 = 0.7062$, n = 17. Based on this correlation, the background BTEX (TPH = 0 ppm) was further estimated to be ~ 0.0034 ppm for this contaminated site. The most contaminated source area by BTEX was 4 ppm at the same site (TPH = 950 ppm).

Recently published TPH results were compared with the GC-MS values for the volatile aromatic fraction of BTEX. For studied samples, the ratio of [BTEX]/[TPH] ranged from 0.1% to 1.2% (average) for the samples with TPH values > 100 ppm. Comparison of the ratios of [BTEX]/[TPH] after one year period showed that, for most locations, BTEX fraction apparently was released or degraded faster than other fractions in TPH [20].

Recent results of analyses of river soil and top soil contaminated with unleaded gasoline, diesel fuel, used oil and sludge sample, evaluated by the leaching test (TCLP), are presented in Table 3 [11]. A low organic carbon content of 0.6%

^dAnalyte concentration in leaching test (TCLP) exceeded regulatory limit (0.5 ppm for benzene).

and clay content of 4% characterized the river soil, while the topsoil had 2.3% of organic carbon content and 41% of clay content [11]. The spiking level with unleaded gasoline greater than 1000 ppm in river soil exceeded the TCLP regulatory threshold level for benzene (0.5 ppm) (e.g., for 5000 ppm spike, TCLP = 1.66 ppm, for 10000 ppm spike, TCLP = 2.38 ppm). Diesel fuel contaminated soils did not exceed the regulatory limits in any contamination level studied. The results indicated that there were significant differences in the leaching efficiency of TCLP, which depends on soil having natural organic matter and the extent of contamination.

The performance of the GC-MS method 8020B [16] was compared with IR-spectroscopy method 418.1 [9] to quantify hydrocarbons in samples collected from a site contaminated by transformer oil [21]. The comparison illustrated that measurements by IR-spectroscopy produced a higher overall estimate of hydrocarbons while GS-MS resulted in lower values. The results obtained with both methods were compared using Freon-113 (with IR quantification) and methylene chloride (with GC-MS quantification) as the extraction solvent. The consensus means obtained with (GC-MS) are typically 28% to 57% lower than those found with IR-spectroscopy.

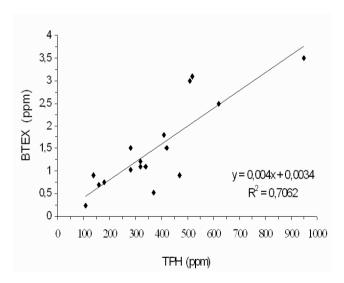


Fig. 1. Correlation between volatile aromatic fraction (BTEX) and total petroleum hydrocarbons (TPH) in contaminated soil samples

Recent results of analyses of river soil and top soil contaminated with unleaded gasoline, diesel fuel, used oil and sludge sample, evaluated by the leaching test (TCLP), are presented in Table 3 [11]. A low organic carbon content of 0.6% and clay content of 4% characterized the river soil, while the topsoil had 2.3% of organic carbon content and 41% of clay content [11]. The spiking level with unleaded gasoline greater than 1000 ppm in river soil exceeded the TCLP regulatory threshold level for benzene (0.5 ppm) (e.g., for 5000 ppm spike, TCLP = 1.66 ppm, for 10000 ppm spike, TCLP = 2.38 ppm). Diesel fuel contaminated soils did not exceed the regulatory limits in any contamination level studied. The results indicated that there were significant differences in the leaching efficiency of TCLP,

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3.3.TPH health assessments

Despite the large number of hydrocarbons found in petroleum products, only a relatively small number of them have been characterized for toxicity [5]. The health effects of some fractions can be fully characterized based on their components or representative compounds (e.g., light aromatic BTEX fraction (benzene, toluene, ethylbenzene, and xylenes) and naphthalene. The Agency for Toxic Substances and Disease Registry (ATSDR) does not assess cancer potency for TPH components, and only for some components toxicological information is provided, e.g., minimal risk level (MRL) [22].

Health effects that are common to the BTEX are of neurological nature. Benzene has hematological effect and is classified in EPA Group A (human carcinogen). The inhalation minimal risk level for each of the BTEX compounds (acute MRL) was determined: benzene 0.05 ppm, toluene 3.0 ppm, o-, m-, and p-xylene 1.0 ppm, and ethylbenzene 0.2 ppm [5].

For gasoline, kerosene, and jet fuels, commonly selected hydrocarbon chemicals of concern are benzene, toluene, ethylbenzene, and (BTEX). Additional chemicals of concern for kerosene and jet fuels are polycyclic aromatic hydrocarbons (PAHs). For diesel fuel, light fuel oils, and heavy fuel oils, the commonly selected hydrocarbon chemicals of concern are PAHs. Twelve PAHs, including benzo(a)pyrene, were selected for consideration [5].

4. Conclusions

It should be stressed that the results obtained using TPH methods other than gas chromatography (GC) must be interpreted with caution because the potential risk posed by BTEX compounds may not be adequately addressed. The gas chromatography-flame ionization detector (GC-FID) methods appear to offer the best hope for standard TPH tests in soil and groundwater verification of site cleanup. The (GC-MS) is currently the most advanced and comprehensive technique for evaluation of petroleum compounds in the environment. The increased solubility of the BTEX chemical components from gasoline mixtures can thus more likely result in groundwater contamination. High TPH test results may require action on the

part of land owners, local or state governments, and engineering firms called on to remove or reduce the TPH problem [23-26].

When soil parameter TPH is greater than 500 mg/L but BETX contaminants level are below subsurface soil risk (0.26 mg/kg benzene, 200 mg/kg ethylbenzene, 170 mg/kg toluene and 1900 mg/kg total xylenes), and polynuclear aromatic hydrocarbon (PAH) (e.g. benz(α)antracene, benzo(α)pyrene, polychlorinated biphenyl, PCBs) concentrations are below potential exposure, the contaminated soil is left for natural biodegradation. Preventing spills and implementing best management practices for used petroleum oil and O/G generators can keep our environment clean and safe.

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