Product Chemistry Science Chapter on

Creosote

Chemical Overview

Chemical Name:	Coal Tar Creosote
Common/Trade Name:	Creosote, P1/P13, P2
Chemical Family:	Distillate mixture obtained from bituminous coal
CAS Registry Number:	8001-58-9
OPP Chemical Code:	025004
Molecular Formula:	Not Applicable

Heavy Duty Wood Preservative **Creosote** is a heterogeneous mixture of polycyclic aromatic hydrocarbons and other heteronuclear aromatic substances. US EPA 's document **Guidance for the Reregistration of Pesticide Products Containing *CoalTar/Creosote*** (Document 540-RS-88-066)[1] recognizes that "hundreds of individual chemicals have been identified in coal tar/creosote and Lorenz & Gjovik[2] and McNeil[3] have identified eight classes of compounds commonly found in creosote and coal tar products." These are listed as follows:

1. Non-substituted six-membered rings
2. Heterocyclic nitrogen bases
3. Heterocyclic oxygen and sulfur compounds
4. Alkyl substituted compounds(including polycyclic rings)
5. Hydroxy compounds
6. Aromatic amines
7. Paraffins
8. Naphthenes

Creosote as a pesticide used for wood preservation has no manufacturing source. This Science Chapter deals with the Creosote mixture solution derived from tar which is produced from carbonization of bituminous coal. This is a coal tar fractional distillation process and from this two fractions namely **P1/P13 and P2** are obtained. In general fractions are collected when the temperatures are between 210 ^{o} C and 355 ^{o} C.[4]

Creosote Council, which represents the Creosote Industry, submitted the product

chemistry data for the P2 and P1/P13 creosote fractions in 1992 and resubmitted the data again in 1999 in compliance to the EPA's Reregistration Standard and Data-Call-In issued for pesticide products containing coal tar creosote. In the absence of EPA methodology to determine the physical/chemical characteristics of mixtures like creosote fractions, the Industry has supplied the data based on the analysis performed by using the methods described by the American Wood Preservers Association (AWPA) Standard Method for Analysis of Creosote and Oil-Type Preservatives, specifically to analyze the creosote P2 and P1/P13 fractions for determination of xylene insolubles, determination of specific gravity, distillation fractions and determination of water content in the respective fractions.

AWPA has stated that the P1/P13 and P2 (creosote)fractions for use as heavy duty wood preservatives 'shall be a pure coal tar product, derived entirely from tar produced by carbonization of bituminous coal. Carbonization of coal is accomplished by distlling coal and coal tar fraction is collected. The coal tar fraction itself consists of: light oil, middle oil and heavy (oil) anthracene. It is the middle oil fraction that is further distilled and various fractions from this distillation are collected between the temperatures of 210 ^{o} and 355 ^{o} C.

Open literature search shows (James Mueller et. al)[5] soil contaminated with coal tar creosote consists of: 85% polycyclic aromatic hydrocarbons (PAHs), 10% phenolic compounds and 5% N-, S-, and O- heterocyclics. Table 1 lists some Polycyclic aromatic hydrocarbons found in the P2 and P1/P13 fractions of creosote and have been reported by the Creosote Council in its product chemistry data submissions. Table 2 lists the phenolic compounds and Table 3 lists the heterocyclic compounds [5]. These components of Tables 1,2 and 3 represent 95% of the total constituents in coal tar creosote. It must be pointed out that among the PAHs listed in Table 1, sixteen are on the EPA's List of Priority Pollutants.

Table 1

Polycyclic Aromatic Hydrocarbons (PAHs) in Coal Tar Creosote

Compound	*Relative Percentage*	*Molecular Weight*
Naphthalene	**13**	**128.2**
2-Methylnaphthalene	**13**	**142.2**
Phenanthrene	**13**	**178.2**
Anthracene	**13**	**178.2**
1-Methylnaphthalene	**8**	**142.2**
Biphenyl	**8**	**154.2**
Fluorene	**8**	**166.2**
2,3-Dimethyl naphthalene	**4**	**156.2**
2,6-Dimethyl naphthalene	**4**	**156.2**
Acenaphthene	**4**	**154.2**
Fluoranthene	**4**	**202.3**
Chrysene	**2**	**228.2**
Pyrene	**2**	**202.3**
Antraquinone	**1**	**208.2**
2-Methyl anthracene	**1**	**192.3**
2,3-Benzo[b]fluorene	**1**	**216.3**
Benzo[a]pyrene	**1**	**252.3**

Table 2
Phenolic Constituents in Coal Tar Creosote

Compound	*Relative Percentage*	*Molecular Wt.*
Phenol	**20**	**94.1**
o-Cresol	**10**	**108.1**
m-Cresol	**10**	**108.1**
p-Cresol	**10**	**108.1**
Pentachlorophenol	**10**	**266.4**
2,5-Xylenol	**7.5**	**122.2**
3,5-Xylenol	**7.5**	**122.2**
2,3-Xylenol	**5**	**122.2**
2,4-Xylenol	**5**	**122.2**
2,6-Xylenol	**5**	**122.2**
3,4-Xylenol	**5**	**122.2**
2,3,5-Trimethylphenol	**5**	**136.0**

Table 3
Heterocyclics in Coal Tar Creosote

Compound	*Relative Percentage*	*Molecular Wt.*
Heterocyclics & N-Containing Aromatics:		
Quinoline	**10**	**129.2**
Isoquinoline	**10**	**129.2**
Carbazole	**10**	**167.2**
2,4-Dimethylpyridine	**10**	**107.2**
Acridine	**5**	**179.2**
Aniline	**5**	**93.1**
2-Methyl quinoline	**5**	**143.2**
4-Methyl quinoline	**5**	**143.2**
Pyrrole	**5**	**67.1**
Pyrrolidine	**5**	**71.2**
S-Heterocyclics:		
Benzo[b]thiophene	**10**	**134.2**
Dibenzothiophene	**10**	**184.3**
O-Heterocyclics:		
Dibenzofuran	**10**	**168.2**

Table 4
Analytical Results of Creosote P2 and P1/P13 Fractions

Molecular ion (M^+)	Compound	CAS #	P2 fraction % (mean)	P1/P13 fraction % (mean)
117	Indole	120-72-9	0.20	
	Indene		0.5	NC
128	Naphthalene	91-20-3	17.3	6.2
129	Quinoline	91-22-5	0.50	1.0
134	Benzo[c]thiophene		0.40	NC
142	1-Methylnaphthalene	90-12-0	1.3	2.5
142	2-Methylnaphthalene	91-57-6	2.80	5.6
154	Biphenyl	92-52-4	0.71	1.6
154	Acenaphthene	83-32-9	4.40	7.7
156	Naphthalene	91-20-3	17.3	6.2
156	1,3-Dimethyl naphthalene	575-41-7	0.60	0.80
166	Fluorene	86-73-7	4.03	6.0
167	9H-Carbazole	86-74-8	1.4	1.7
168	3-Methyl biphenyl (3-phenyl toluene)	643-93-6	0.61	0.30
168	Dibenzofuran	132-64-9	2.3	4.3
	1-Ethylnaphthalene		0.50	0.60
178	Phenenthrene	85-01-8	9.60	12.8
178	Anthracene	120-12-7	2.90	3.1
179	Benzoquinoline-1(7,8-benzoquinoline)	230-27-3	0.70	
180	9H-Fluorene		3.5	6.0
182	4-Methyldibenzofuran		0.40	0.80

Molecular ion (M^+)	Compound	CAS #	P2 fraction % (mean)	P1/P13 fraction % (mean)
184	Dibenzothiophene	132-65-0	0.94	1.3
190	4H-Cyclopenta[def]phenanthrene	203-64-5	1.74	1.5
	Pyrene		4.0	4.7
192	2-Methylphenanthrenes		0.60	
	Chrysene		0.10	1.4
202	Fluoranthene	206-44-0	4.60	5.5
202	Pyrene(benzo[def]phenanthrene	129-00-00	3.64	
204	2-Phenylnaphthalene	-	0.47	0.20
	Benz[e]pyrene		0.50	0.3
	Benzo[ghi]perylene		0.10	<0.1
216	1,2-Benzofluorene(benzo[a]fluorene	-	0.73	
216	2,3-Benzofluorene	243-17-4	0.80	0.90
	Methylpyrene		0.30	0.20
228	Benz[a]anthracene	56-55-3	0.20	0.40
228	Chrysene(benz[a]phenanthrene)	218-01-9	1.4	
252	Benz[b]fluoranthene	205-99-2	0.51	0.80
	Benzo[a]pyrene			0.40

Notes:

1. As most of the creosote constituents are polyaromatic hydrocarbons (PAHs) and solubilities in water or non-aqueous media is not high, exact and accurate quantitation is not possible. The registrants conducted a quantitation method for the PAHs based on the calibration curves generated on four PAHs: naphthalene, (two ring compound), phenanthrene (3 ring compound) and two four ring compounds: pyrene and chrysene. Calibaration curves were generated for these substances over a concentration range of 2 to 1000µg/ml. These substances work as markers for lesser known and identified PAHs in the creosote fractions. First GC was used to separate the components and then quadruple Mass Spectrometry was to obtain the mass

spectra of individual substances. The registrants reported the presence of components to levels less than 0.10%. The Table 4 identifies the components that are over 0.10 % in both the P2 and P1/P13 fractions. The list also includes the presence of non-PAH components

Science Assessment

The Agency reviewed the data submitted by the registrants and an open literature search was also performed for the purpose of determining the Reregistration eligibility of creosote as a wood preserving pesticide.

Product Chemistry Assessment

The physical and chemical properties of both distillate fractions creosote P1/P13 and P2 are described in the following

P1/P13 Fraction

Chemical Name:		Coal Tar Creosote
Molecular Wt.:		No Applicable
Color:		2.5Y2/2 to 2.5Y4/2 (Based on Munsell color scheme)
Odor:		Sharp, aromatic, wood-like
Solubility:		313 µg/ml
Vapor Pressure:		11.1 mm Hg at 24.4 °C
Log P:	3.247	
Stability:		Short term(accelerated)stability was performed on four constituents of the mixture: naphthalene, phenanthrene pyrene and chrysene for a period of 30 days at 60 ° C. At the end of thirty day period, naphthalene remaining was : 96.5%, phenanthrene: 87.2%, pyrene: 86.9% and chrysene: 92.4%
Viscosity;		14.60 mm/s
Storage Stability:		Not determined.

Notes:

1. The P1/P13 samples, provided by the Industry to Research Triangle Institute, were distilled, within 95% confidence limit, residues remaining were less than 1.1% as required by the AWPA Standard A1-91 (This test is similar to the EPA's Certified Limit Test required for other pesticides).
2. Insoluble mass in Xylenes: Duplicate determinations showed that this fraction contained between 0.21 to 0.23% insoluble materials.

3. Specific gravity of the fraction, for the industry sample (single determination) is 1.0934 (corrected to 38ºC)
4. Moisture (water) content for the industry sample (single determination) is 0.4%.

All these results were obtained by using the AWPA Method A1-91 Series.

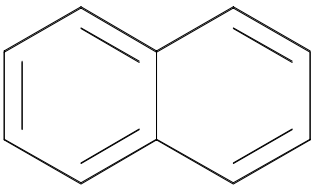
P2 Fraction

Chemical Name:	Coal Tar Creosote
Color:	10YR2/1 to 2.5Y5/5 (Munsell color scheme)
Odor:	Strong aromatic, Petroleum-like
Solubility:	306 µg/ml
Vapor Pressure:	8.6 mm Hg at 24.4 to 24.5 ºC
Log P	3.311
Stability:	
Viscosity:	15.5 mm/s at 25 ºC
Storage Stability:	Short-term (accelerated study, 30 days, at 60ºC) stability study was performed on four PAHs: naphthalene, phenanthrene, pyrene and chrysene; at the end of thirty day period the percent decline for naphthalene was 89.3%, phenanthrene: 88.4%, pyrene: 90.2% and chrysene: 92.9%.

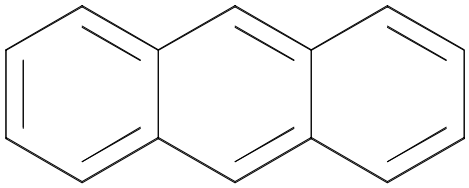
Note:
1. The amounts of residues left after the distillation process is less than 1.1% as required by the AWPA Standard A1-91 (This test is similar to the EPA's Certified Limit Test required for other pesticides).
2. Insoluble mass of xylenes duplicate determination showed that this fraction contained 0.32% insoluble materials (relative amounts).
3. The specific gravity for the industry sample(single determination) is 1.0934 (corrected to 38ºC).
4. Moisture(water) content for the industry sample(single determination) is 0.15% by volume

The chemical structure of sixteen PAHs (EPA Priority Pollutants) are provided below in the order of increasing complexity.

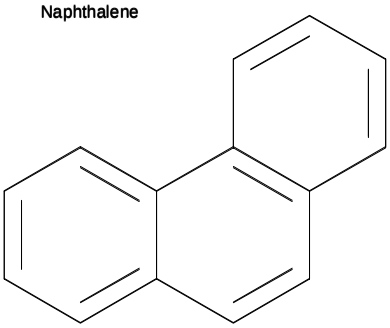
Chemical structures of PAHs in the order of increasing complexities



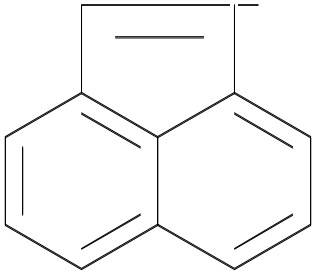
Naphthalene



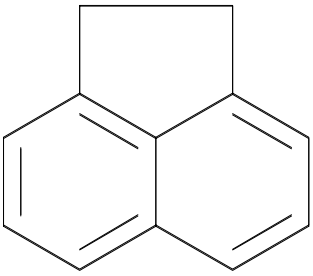
Anthracene



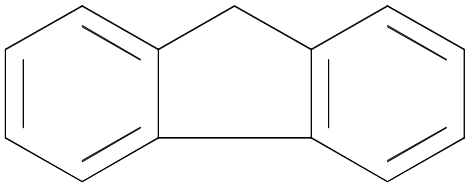
Pheananthrene



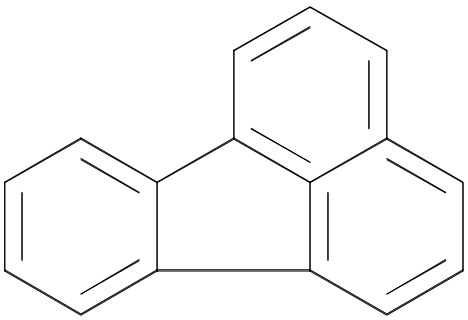
Acenaphthylene



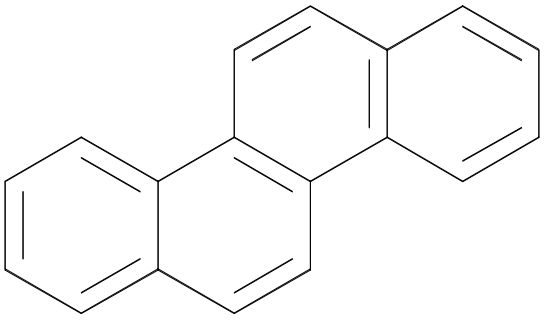
Acenaphthene



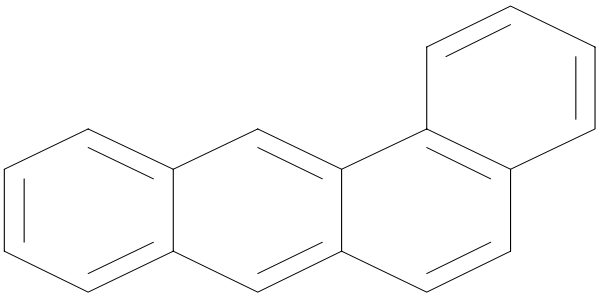
Fluorene



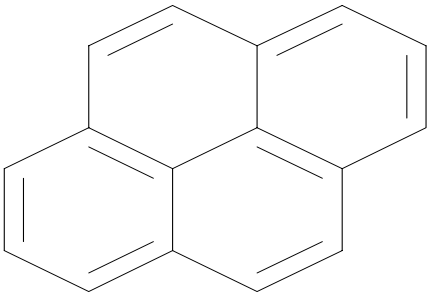
Fluoranthene



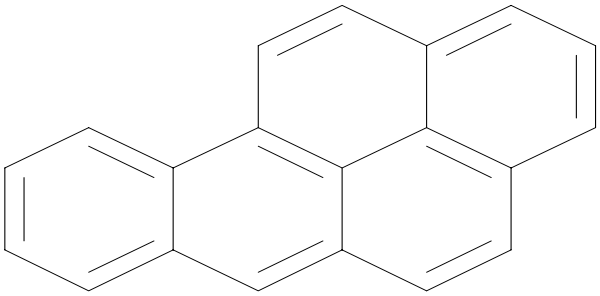
Chrysene



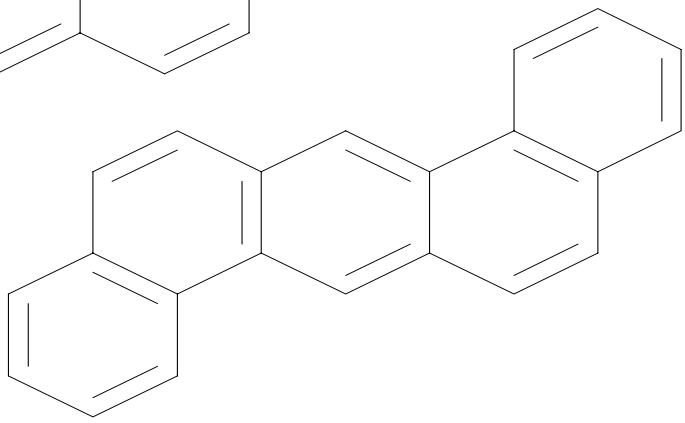
Benz[a]anthracene



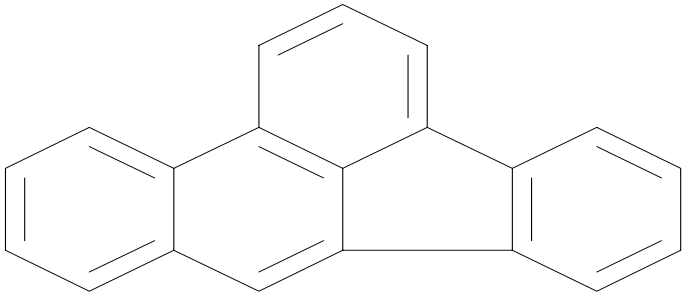
Pyrene



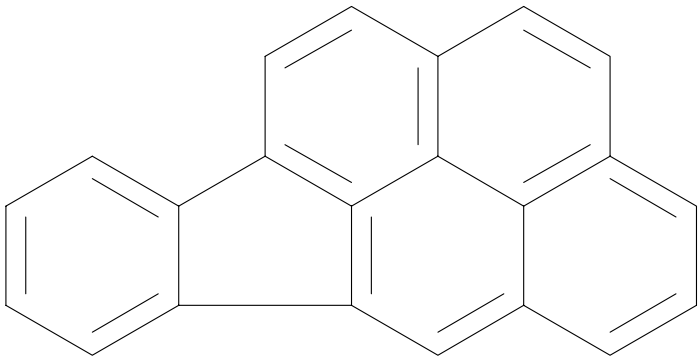
Bnez[a]pyrene



Dibenz[a,h]anthracene

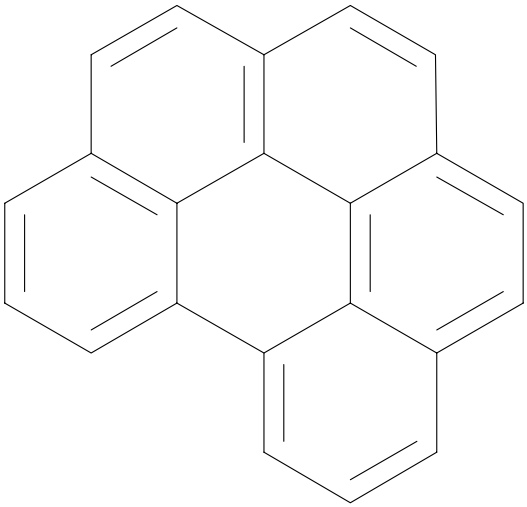


Benz[b]fluoranthene



Indeno[1,2,3-cd]pyrene

Some of the physical properties of selected PAHs are listed in Table 6 (Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals by D. Mackay et al., Lewis Publishers, 1992). Many of these are measured and a number of them (particularly the K_{OW}) are estimated values.



Bnez[g,h,i,]perylene

Table 6

SELECTED PHYSICO-CHEMICAL PROPERTIES OF PAHs AT 25^{O}C

Compound	v.p (s), mm Hg	Log K_{OC}	Solubility mg/L	log K_{OW}	Henry Law constant Pa m^3/mol
Indan	15.1	-	0.10	3.33	232.82
Naphthalene	7.8×10^{-2}	3.29	3.1×10^{-2}	3.37	43.01
1-Methyl Naphthalene	6.6×10^{-2}	2.96	2.8×10^{-2}	3.87	44.90
2-Methyl Naphthalene	6.7×10^{-2}	3.93	2.5×10^{-2}	3.86	51.19
Biphenyl	9.97×10^{-3}	3.57-3.77	7×10^{-3}	3.90	28.64
Bibenzyl	3.0×10^{-3}	-	4.3×10^{-3}	4.70	16.93
Acenaphthene	2.2×10^{-3}	3.79	3.8×10^{-3}	3.92	12.17
Acenaphthylene	6.7×10^{-3}	3.75, 3.83	1.6×10^{-2}	4.00	8.40
Fluorene	6.7×10^{-4}	3.76	1.9×10^{-3}	4.18	7.87
Phenanthrene	1.5×10^{-4}	4.42	1.1×10^{-3}	4.57	3.24
Anthracene	7.5×10^{-6}	4.42	4.5×10^{-5}	4.54	3.96
Pyrene	4.5×10^{-6}	4.92	1.3×10^{-4}	5.18	0.92
Fluoranthene	9.0×10^{-6}	4.74	2.6×10^{-4}	5.22	1.037
Benzo[a]fluorene	-	-	4.5×10^{-5}	5.40	
Benzo[b]fluorene	-	-	2.0×10^{-6}	5.75	
Chrysene	4.2×10^{-9}	4.89	-	1.649	5.86
Benz[a]anthracene	2.0×10^{-5}	4.57	1.1×10^{-5}	5.91	0.581
Benzo[a] pyrene	5.2×10^{-9}	5.48	3.8×10^{-6}	6.04	0.046
Benzo[e] pyrene	5.5×10^{-9}	4.00	4.0×10^{-6}		0.020
Perylene	1.0×10^{-9}	-	4.0×10^{-7}	6.25	0.003
Benzo[b]fluoranthene	-	5.74	1.5×10^{-6}	5.80	-
Benzo[k]fluoranthene	3.9×10^{-9}	5.92	8.0×10^{-7}	6.00	0.016
Benzo[ghi]perylene		6.20	2.6×10^{-7}	6.50	0.075

SELECTED PHYSICO-CHEMICAL PROPERTIES OF PAHs AT 25^{O}C					
Dibenz[ah]anthracene	2.7 x 10^{-12}	6.52	6.0x10^{-7}	6.75	-

Storage Stability and Corrosion Characteristics

Four ingredients of creosote (naphthalene, phenanthrene, pyrene, and chrysene) were chosen as markers for creosote in determining storage and corrosion stability characteristics for P1, P2, and P1/P13 fractions of creosote. Specifically, creosote fractions studied were:

P1, P2, and P1/P13 naphthalene;
P1, P2, and P1/P13 phenanthrene;
P1, P2, and P1/P13 pyrene; and
P1, P2, and P1/P13 chrysene

Storage Stability

In storage stability studies, mean concentrations of P1, P2, and P1/P13 fractions of napthalene, phenanthrene, pyrene, and chrysene at one year (represented as percent of initial mean concentrations at day zero) ranged from 92.7% - 104.0%, 93.2% - 112.0%, 85.3% - 108.0%, and 70.1% - 84.7%, respectively, after one year of storage. These data indicate that napthalene, phenanthrene, pyrene fractions remained stable over a period of one year, whereas chrysene fractions declined from 15.3% - 29.9% over the same time period.

Corrosion Characteristics

In corrosion characteristic studies, mean concentrations of P1, P2, and P1/P13 fractions of napthalene, phenanthrene, pyrene, and chrysene at one year (represented as percent of initial mean concentrations at day zero) ranged from 95.9% - 109.0%, 101.0% - 114.0%, 96.3% - 110.0%, and 74.5% - 88.5%, respectively, after one year of study. These data indicate that napthalene, phenanthrene, pyrene fractions remained stable over a period of one year, whereas chrysene fractions declined from 11.5% - 25.5% over the same time period.

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MRID	CITATION
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