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Characterization of Three Creosotes as Potential Soil and Aquifers Contaminants

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ABSTRACT

Creosote, as a distillation by-product, contains a very high complex mixture of hydrocarbons and metals. It has been reported that polyaromatic hydrocarbons PAHs, phenols and many metals are present in high concentrations in those fluids, though there is a big lack of data in literature. In this work, three creosotes (dark brown, light brown and a Fluka Chemical product) were characterized in terms of the 16 PAHs considered by USEPA as priority pollutants, total phenols content, as well as 10 metals analysed by Inductive Plasma. It was found that industrial and analysis grade creosotes resulted very different. Dark brown creosote has 215,054 mg/kg of total PAHs, while light brown creosote, only 23,690 mg/kg (one tenth). Strangely, the analysis grade product showed no PAHs presence. Regarding phenols, dark brown, light brown and analytical grade products showed contents of 1,205, 2,777 and 348,215 mg/kg, respectively. Many metals were found in all the samples. These data are very important for environmental forensic applications. It is very important to underline that from the 16 PAHs considered by USEPA, 5 are considered as carcinogenic. Besides, the presence of phenols and metals, make creosote a very harmful product.

Keywords: Contamination, Creosote, Metals, Phenols, PAHs and Soils.

INTRODUCTION

Creosotes are by-products of crude distillation. These wastes are formulated, by dilution in mineral oil and with addition of phenols, such as trichlorophenol and pentachlorophenol. Creosote is used mainly for painting railway sleepers, with biodegradation inhibition purposes [(1)]. Also, creosote is employed for painting wood, which is in contact with water in coasts, lagoons, and rivers and many other applications. Creosote, as a distillation by-product, contains a very high complex mixture of hydrocarbons and metals. It has been reported that polyaromatic hydrocarbons PAHs, phenols and many metals are present in high concentrations in those fluids, though there is a big lack of data in literature. It has been reported the presence in creosote of cresols, phenol, pentachlorophenol, xylenols, PAHs, quinoline, isoquinoline, carbazole, 2,4-dimetylpyridine, and dibenzofurane, among others. Creosote and pentachlorofenols have been employed in wood sites, causing soil and water contamination[(2,3)].

Some authors have reported remediation techniques for creosote contaminated soils, such as bioremediation[(4,5)] , surfactant enhanced biodegradation[(6)], composting[(7)], soil washing followed by slurry-phase bioreactors[(8)], and Fenton´s reagent followed by microbial treatment and surfactants[(9)] and using vegetation[(10)] among others. First step in a remediation program is the knowledge of contamination level and distribution. Many times, the first problem is the lack of data, regarding the hydrocarbon fractions characteristics. Very few papers have deal with the characterization of creosote in terms of their hazardous components[(11)].

Our research group is focused on the study of soils and aquifers contamination as well as developing of remediation techniques. We have previously reported the characterization of a Mexican crude and five oil fractions (including diesel, gasoil, two gasolines and a fuel oil[12] as well as the characterization of soils contaminated with light, medium and heavy Mexican crudes[13]. This work has been focused on environmental forensic applications.

Other works reported recently by our research group has been aimed to the proposal of cleaning technologies for contaminated soil, either by the presence of petroleum components, metal presence or both [14,15].

More recently, we have studied the emulsification of creosote (as model of other DNAPLs), using bentonite particles for emulsion stabilization in presence of the right amounts of NaCl and CTAB, as a feasible remediation technique for contaminated aquifers[16]. In that work, we have used the dark creosote characterized in this work.

The aim of this work was the characterization of three creosotes (two of commercial origin and one of reagent grade) in terms of the phenols, PAHs and metals content, since creosote is a complex compound which may be found as contaminant in soils and aquifers.

MATERIALS AND METHODS

Three creosote samples were analyzed in terms of the 16 PAHs considered by USEPA as priority pollutants, total phenols and some metals. Dark brown and light brown creosote are commercial products from the company Wickes Building Supplies Limited, (UK). Light brown product is a LNAPL, while dark brown creosote is a DNAPL. The third creosote is an analysis product from Fluka (USA). Analysis of PAHs, metals and total phenols were carried out in accord with EPA 8270D-1988, EPA 9066-1986 and EPA 6010-1996 methodologies, respectively .

RESULTS

Table 1 show the results regarding the PAHs characterization carried out with the three creosote samples. As noted, Dark and light brown creosotes showed the presence of high amounts of PAHs (the 16 considered as USEPA priority compounds), but the Fluka creosote did not show the presence of any one. PAHs found in higher concentration at the dark brown product were phenanthrene (50,940 mg/kg) fluorene (32,687 mg/kg), acenaphthene (29,311 mg/kg), pyrene (23,560 mg/kg), naphthalene (20,625) and acenaphthylene (11,061 mg/kg). The rest of the present PAHs were fluoranthene (4,141 mg/kg), anthracene (2,852 mg/kg), chrysene

(2,270 mg/kg), and finally benzo(a)anthracene (301.2 mg/kg). Total found PAHs were equivalent to 177, 750.8, that means 17% of the whole sample. One important thing to underline is the presence of carcinogenic compounds. From the listed PAHs, only benzo(a)anthracene and chrysene, are considered carcinogenic, and they were present in quite high concentrations.

In the case of light brown creosote, PAHS found at higher concentrations were naphthalene (18,937 mg/kg), phenanthrenes (1,843 mg/kg), and fluorene (1,207 mg/kg). Lower concentrations of acenaphthene (756 mg/kg), fluoranthene (379 mg/kg), pyrene (412 mg/kg) and anthracene (149.1 mg/kg) were also found, giving a total PAHs content of 23,864.9 mg/kg. None of the PAHs considered as carcinogenic were found at this sample. According to the total PAHs concentration, it seems that dark brown creosote is 7.5 times more concentrated than the light brown one.

None of the 16 PAHs were found for the Fluka creosote. In fact the dark and light brown creosotes are products showing a brown color and some viscosity, while Fluka product is clear and less viscous. The characteristic stringent odor of creosote is present in the three samples. Regarding the phenols concentration, the dark brown creosote showed a total amount of 1,205 mg/kg, while light brown creosote and the Fluka products gave values of 2,777 and 348,215 mg/kg, respectively.

On table 2, a comparison of dark brown creosote with other hydrocarbons is shown. In the same table, PAHs concentrations for the 16 USEPA compounds for creosote, Tabasco crude, and gasoline Magna, as well as the ranges reported for condensates and crudes by McMillen *et al*. (2001). It is clear that the product with a higher PAH content is dark brown creosote, followed by the Tabasco crude and gasoline Magna, at the end. Tabasco crude showed presence of benzo(a)anthracene (627 mg/kg), benzo(b)fluoranthene (224 mg/kg), benzo (g,h,i)perylene (110 mg/kg), benzo(k)fluoranthene (25 mg/kg), benzopyrene (19 mg/kg), chrysene (434 mg/kg), phenanthrene (465 mg/kg), fluorene (128 mg/kg), and naphthalene (745 mg/kg), giving a total amount of 2,766 mg/kg. Regarding the Gasoline *Magna*, only naphthalene was found at a concentration of only 0.03 mg/kg.

These values are compared with the values reported by McMillen *et al.*[17] for a site contaminated with creosote and the range reported for 26 and crudes. Concentrations found at soil contaminated with creosotes at this work, are higher than those reported for a site contaminated with creosote, by McMillen *et al.*[17]. In the specific case of acenaphthene, it was 888 times higher, while in the case of anthracene, it was only 8.5 times. On the other hand, chrysene, phenanthrene and fluoranthene resulted 3.7, 32, and 6 times. Finally, fluorene, naphthalene, and pyrene resulted 50, 15 and 36 times, respectively. While the dark creosote showed a total PAH concentration of

215,054 mg/kg, the mean concentration for the creosote-contaminated site[17] showed a concentration of 5,863 mg/kg. Regarding the PAHs values reported for 26 crudes, differences are quite higher, which is expectable, since crudes always show a lower PAH concentration than the distillation-produced fractions such as coal tars.

Regarding the metals concentration present in the creosote samples, it can be said the following. Ten metals were evaluated in the samples. The product showing a higher metal concentration was light brown creosote (538 mg/kg), followed by the dark brown product (325 mg/kg) and the Fluka product at the end (292 mg/kg). All products showed the presence of Ag, Cd, Cr, Pb and Se. In addition, dark and light brown creosotes showed presence of Zn. Levels were as follows. The most abundant metal present in dark brown creosote was Cd (99 mg/kg), followed by Se (83 mg/kg), Pb (81 mg/kg), and Ag (26 mg/kg). Smaller amounts of Cr (19 mg/kg) and Zn (16 mg/kg) were also found.

At the light brown product, the most abundant metal was Cd (130 mg/kg) followed by Cr (110 mg/kg), Se (105 mg/kg), Ag (87 mg/kg), and Pb (85 mg/kg). Smaller amounts of Zn (19 mg/kg) were also found. The Fluka product showed a high concentration of Cd (117 mg/kg), followed by Se (77 mg/kg), Pb (62 mg/kg), and Ag (20 mg/kg). Smaller amounts of Cr (14 mg/kg) were detected.

As expected, in general, metals amounts found at the three creosote samples are higher than those reported for 60 crudes reported in the literature[17], as showed at table 3. Creosotes as a distillation product, tend to accumulate all kind of undesirable compounds, such as PAHs, metals, sulfurated and nitrogenated compounds, etc.[18].

All these results are extremely useful for environmental forensic applications. It is important to underline the concern that PAHs and metal’s presence on earth and waters. Some of the PAHs found in both dark and light brown creosotes have been reported as carcinogenic.

CONCLUSIONS

Dark and light brown creosotes showed the presence of high amounts of PAHs (the 16 considered as USEPA priority compounds), but the Fluka creosote did not show the presence of any one. PAHs. PAHs found in higher concentration at the dark brown product were phenanthrene fluorene, acenaphthene, pyrene, naphthalene and acenaphthylene. The rest of the present PAHs were (in minor proportions) fluoranthene, anthracene, chrysene, and finally benzo(a)anthracene. Total found PAHs were equivalent to 177, 750.8, that means 17% of the whole sample. In the case of light brown creosote, PAHS found at higher concentrations were naphthalene, phenanthrenes, and fluorene. Lower concentrations of acenaphthene, fluoranthene, pyrene and anthracene were also found, giving a total PAHs content of 23,864.9 mg/kg. None of the PAHs considered as carcinogenic were found at this sample. According to the total PAHs concentration, it seems that dark brown creosote is 7.5 times more concentrated than the light brown one.

Regarding the phenols concentration, the dark brown creosote showed a total amount of 1,205 mg/kg, while light brown creosote and the Fluka products gave values of 2,777 and 348,215 mg/kg, respectively. The product showing a higher metal concentration was light brown creosote (538 mg/kg), followed by the dark brown product (325 mg/kg) and the Fluka product at the end (292 mg/kg). All products showed the presence of Ag, Cd, Cr, Pb and Se. The most abundant metal present in dark brown creosote was Cd (99 mg/kg), followed by Se (83 mg/kg), Pb (81 mg/kg), and Ag (26 mg/kg). Smaller amounts of Cr (19 mg/kg) and Zn (16 mg/kg) were also found. At the light brown product, the most abundant metal was Cd (130 mg/kg) followed by Cr (110 mg/kg), Se (105 mg/kg), Ag (87 mg/kg), and Pb (85 mg/kg). Smaller amounts of Zn (19 mg/kg) were also found.

The Fluka product showed a high concentration of Cd (117 mg/kg), followed by Se (77 mg/kg), Pb (62 mg/kg), and Ag (20 mg/kg). Smaller amounts of Cr (14 mg/kg) were detected. All these results are extremely useful for environmental forensic applications. It is important to underline the concern that PAHs and metal’s presence on earth and waters. Some of the PAHs found in both dark and light brown creosotes have been reported as carcinogenics.

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Table 1. PAHs and total phenols for the dark, light and Fluka creosotes. All values in mg/kg.

Compound	Dark creosote	Light creosote	Fluka creosote
Acenaphthene	29,311.30	755.80	ND
Acenaphthylene	11,061.50	ND	ND
Anthacene	2,852.60	149.10	ND
a) Benzo(a)anthracene	301.20	ND	ND
b) Benzo(b)fluoranthene	ND	ND	ND
Benzo(g,h,i)perylene	ND	ND	ND
c) Benzo(k)fluoranthene	ND	ND	ND
d) Benzo(a)pyrene	ND	ND	ND
e) Chrysene	2,270.20	ND	ND
f) Dibenzo(a,h)anthracene	ND	ND	ND
Phenanthrene	5,0940.80	1,843.00	ND
Fluoranthene	4,141.00	379.70	ND
Fluorene	32,687.30	1,207.70	ND
g) Indene(1,2,3,c-d)pyrene	ND	ND	ND
Naphthalene	20,624.90	18,937.00	ND
Pyrene	23,560.00	412.60	ND
Total PAHs	177,750.8	23,684.9	ND
Total phenols	1,205.46	2,777.33	348,215.47

In ***black italics***, compounds considered as carcinogenic.

Table 2. Comparison of PAHs present in dark creosote, Tabasco crude, gasoline and ranges reported for crudes and All values in mg/kg.

Compound	**Dark creosote**	**Tabasco crude***	**Gasoline 2) *Magna*****	**Range in 26 crudes*****	**Soil conc.. creosote production sites mean (mg/kg)*****
Acenaphthene	29,311.30	ND	ND	ND-58	33
Acenaphthylene	11,061.50	ND	ND	ND	-
Anthracene	2,852.60	ND	ND	ND-17	334
Benzo(a)anthracene	301.20	627.63	ND	ND-38	-
Benzo(b)fluoranthene	ND	224.00	ND	ND -14	-
Benzo(g,h,i)perylene	ND	109.94	ND	ND-9.6	-
Benzo(k)fluoranthene	ND	25.59	ND	ND -7	-
Benzopyrene	ND	19.17	ND	ND-7.7	-
Chrysene	2,270.20	434.01	ND	4-120	614
Dibenzo(a,h)anthracene	ND	ND	ND	ND-9.2	-
Phenanthrene	5,0940.80	465.38	ND	ND-916	1,595
Fluoranthene	4,141.00	ND	ND	ND-26	682
Fluorene	32,687.30	127.78	ND	1.4-380	650
Indene(1,2,3,c-d)pyrene	ND	ND	ND	ND-1.7	-
Naphthalene	20,624.90	745.49	0.03	1.2-3,700	1,313
Pyrene	23,560.00	ND	ND	ND-82	642
Total PAHS	215,054	2,776.00	0.03	-	

* Unpublished results, Torres et al (2017), **From: Torres *et al.*, 2003

***From McMillen *et al.*, 2001

Table 3. Metals found at three creosote samples.

Metal	Dark brown creosote	Light brown creosote	Fluka creosote	Range for 26 crudes*
Ag	26.27	87.47	20.11	0.05-0.30
As	<0.2	<0.2	<0.2	ND-0.57
Ba	<0.2	<0.2	<0.2	ND-0.368
Cd	99.18	130.6	117.8	0.003-0.026
Cr	19.79	110.5	14.03	ND-1.43
Fe	<0.2	<0.2	<0.2	NR
Ni	<0.2	<0.2	<0.2	0.05-93
Pb	81.35	85.67	62.72	0.005-0.149
Se	83.04	105.14	77.28	ND-0.52
Zn	16.17	19.32	<0.2	ND-10.9
Total	325.8	538.7	291.94	-

*From McMillen *et al*., 2001.