

EVALUATION OF POLICYCLIC AROMATIC HYDROCARBON CONTENTS IN RELATION TO SEDIMENT AND SOIL PROPERTIES

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAH) sorbed in sediments and soils (s&s) may imply risks to ecosystems and human health since these PAH are often released over time from the porous matrixes of the s&s to the interstitial and surrounding water. Therefore, s&s may act as secondary pollution sources long after traditional remediation actions of s&s have terminated. The physical and chemical characteristics of s&s and the interaction with the PAH would control such accumulation and release. In this study, sediment and soil samples from two contaminated sites were characterized, and their physical, chemical and mineralogical characteristics correlated with the presence of PAH.

Samples of s&s were obtained from the two remediated sites. Particle size distribution, surface area and pore size distribution, mineralogy, organic carbon content, and concentrations of 16 PAH were determined in the samples. K_{ow} for each PAH were related to their presence in the s&s samples. Physical, chemical, and mineralogical characteristics were correlated to the PAH in s&s and recommendations were formulated regarding the need for characterization of s&s in relation to remediation actions of these matrixes to prevent future risks to contaminate ecosystems and affect human health.

Keywords: PAH, Porous Media, Sorption, Soil and Sediment.

INTRODUCTION

When hydrocarbons spill they often accumulate in sediments and soils (s&s). This retention of hydrocarbons depends on the physical and chemical characteristics of the s&s such as texture (particle sizes and porosity) and composition (mineralogy and organic matter content).

The porosity of s&s is divided into voids among particles and inside particles and in both, where water and gases are contained. The pore space refers to the percentage of s&s not occupied by solids. In general, s&s volumes consists of mineral solids, organic matter, and pore space. Pores may be divided in according to their size: macropores and mesopores who are responsible for the circulation of water and air, and micropores who are responsible for storing water in s&s when these are dried. These micropores may also store other substances and contaminants such as hydrocarbons because these have high hydrophobicity. However, as low concentrations of hydrocarbons are achieved in dissolved phase due to degradation, these accumulated hydrocarbons can be slowly released to water, reestablishing new equilibrium conditions. Because of this ability to accumulate and release hydrocarbons, s&s act as potential secondary sources of water pollution [1].

Generally, soil pore sizes are classified according to their diameter, d : micropores ($d < 0.002 \mu\text{m}$) mesopores ($0.002 \mu\text{m} < d < 0.05 \mu\text{m}$) and macropores

($d > 0.05 \mu\text{m}$) [2]. Hydrocarbons can be accumulated in these pores by “sorption”, that is the result of adsorption and absorption; however, in meso- and micropores hydrocarbons may be retained during longer time-periods due to the higher specific surface areas for sorption processes; restrictions of hydrocarbon transport outside these pores, not allowing microorganisms to access these spaces for biodegradation, degrading organisms such as bacteria ($0.5\text{--}5 \mu\text{m}$) are much larger than these pore diameters.

Specific surface areas of s&s are the areas of the solid surfaces per unit mass, including surfaces inside pores. These surfaces are highly reactive and it is where sorption process mainly occur [3]. The sorption capacity in porous media as s&s is directly related with the surface area. Therefore, different authors have observed higher sorption capacities of colloids than s&s for organic contaminants such as benzene, naphthalene, and anthracene [4] and [5].

The solubility of the hydrocarbon greatly influences its ability to be sorbed. Generally, an inverse relationship between the degree of adsorption of a solute and its solubility is observed: for example the adsorption capacity in the sediment increases when the solubility of the hydrocarbon decreases in the aqueous solution [6].

It has also been published the role of the content of organic matter in soils and sediments in the sorption process of polycyclic aromatic hydrocarbons (PAH). The sorption capacity and affinity of the

organic matter depends largely on its composition; some studies report that sorption of PAH is directly related to the content of organic matter in the soil-water system. Furthermore, it has been shown that the sorption of PAH and other hydrophobic organic compounds by soil organic matter is controlled by the polarity of the organic matter [7, 8].

The minerals that make up s&s, contributes to their characteristics, including the pore size distribution. Thus quartz (the most common mineral in s&s due to its natural abundance in rocks) gives the s&s much of its macroporosity (mainly macropores and pores between particles) because it is usually in the form of more or less coarse grains.

Clay minerals play an important role in the texture and physical and chemical characteristics of s&s, giving them plasticity, impermeability, as well as other mechanical properties, and the relationship between s&s and water it contains, especially in its sorption and ion exchange capacities. The texture of the clays involves not only the size of the granules, but also the way they are bound, their orientation in space and compaction [9].

Whereas the presence of PAHs in s&s pose a risk to ecosystems and human health [10], remediation and recovery of these areas represents a challenge for decision makers, because an adequate decrease in PAH concentrations is not always achieved in scheduled times. Cleaning and recovery contracts of contaminated areas tend to be in the order of few months which are often not long to eliminate contaminants accumulated in s&s porous.

Therefore, the aim of this paper is to analyze the relationship between the physical and chemical characteristics of already remediated s&s with the presence of PAH.

METHODOLOGY

For this study sample of s&s from formerly hydrocarbon contaminated areas due to Mexico's oil industry, which have been remedied by Petróleos Mexicanos (PEMEX), were sampled and analyzed.

The sediment samples were obtained from the lagoon "El Yucateco" in the State of Tabasco, in the southeast of the Gulf of Mexico. Samples were collected with an Ekman dredge. Likewise, soil samples were obtained from the ex-refinery "18 de marzo" in Mexico City. The samples were collected with a shovel at about 50 cm deep. The s&s were placed in sealed bags and in glass jars previously cleaned with chromatography-grade acetone, filling up completely the jars to prevent oxidation of the samples with ambient air. Samples were stored at 4 °C and in the dark while they were transported to the laboratory for analysis.

Characterization Of Sediment And Soil Samples

Physical and chemical characterization of the s&s samples were carried out using the methods outlined in table 1.

Table 1. Physical and chemical characterization of soil and sediment samples.

Parameter	Method
Surface area and pore size distribution	Physisorption (Autosorb IQ, model ASIQU00U00-6)
Particle size distribution	Laser diffraction (Beckman Coulter LS230 Small Volume Module Plus)
PAH	EPA8270D-1988 GC/MS (Hewlett Packard 5973 Mass Selective Detector)
TOC	Wet oxidation [11]

The surface area was calculated by the model BET (Brunauer, Emmett and Teller) used as the reference method for determining the specific surface of a solid. The model is obtained from a number of adsorbed molecules needed to cover with a monolayer solid. The pore volume was calculated by the model DFT (Density Functional Theory). This is the mathematical model used to analyze, based on statistical mechanics, the configuration of the adsorbed molecules at the molecular level in meso- and micropores [2].

RESULTS

The characteristics and concentrations of the 16 PAH of environmental interest in the s&s samples are presented in table 2, as well as the sum of these PAH (Σ PAH) (for those PAH whose concentrations that were not detected, half of the quantification limits were considered).

Concentrations of PAH in all samples were below the limits considered Low Effect Level (LEL), compiled and reported by Buchman [12]. The Σ PAH were also lower than the LEL limit defined by Persaud et al. [13] as well as the limits defined by national regulations [14]. Weighting Σ PAH in s&s with the TOC resulted in values that do not exceed the limit Severe Effect Level (SEL) recommended by Persaud and colleagues [up cit.] (Table 2).

Table 2. Characteristics and evaluated results of PAHs in sediment and soil samples.

PAH	MW	Solubility (mg/L) ^[15]	log K _{ow} ^[15]	Sed 1 (µg/kg)	Soil 1 (µg/kg)	Soil 2 (µg/kg)	LEL (sed) ^[12]	LEL (soil) ^[12]
Acenaphthene	154,21	0,0004	3,92	<2,0	<2,0	<2,0	6,71	682.000
Acenaphthylene	152,19	3,9300	4,07	<3,5	<3,5	<3,5	5,87	682.000
Anthracene	178,23	0,7600	4,45	8,82	35,66	67,22	46,9	1.480.000
Benzo(a)anthracene	228,29	0,0100	5,61	11,96	40,08	58,13	74,8	5.210
Benzo(a)pyrene	252,30	0,0016	6,06	<5,4	47,05	62,9	88,8	1.520
Benzo(b)fluoranthene	252,30	0,0012	6,04	<5,0	54,77	67,26	ND	59.800
Benzo(g,h,i)perylene	276,33	0,0003	6,63	<2,8	47,61	0,05	ND	119.000
Benzo(k)fluoranthene	252,30	0,0068	6,12	<3,9	69,92	65,22	ND	148.000
Chrysene	228,30	0,0028	5,56	16,53	46,35	79,72	108,0	4.730
Dibenzo(a,h)anthracene	278,35	0,0005	6,84	<3,1	<3,1	<3,1	6,22	18.400
Phenanthrene	178,20	1,2000	4,45	24,39	38,73	45,49	86,7	120.000
Fluoranthene	202,26	0,2600	4,90	21,27	46,28	89,27	113	122.000
Fluorene	166,22	1,8000	4,18	<3,1	<3,1	<3,1	21,2	122.000
Indeno(1,2,3,c,d)pyrene	276,30	0,0620	6,58	<4,1	42,15	49,36	ND	109.000
Naphthalene	128,17	31,600	3,30	<4,9	41,89	<4,9	34,6	99,4
Pyrene	202,30	0,7700	4,88	39,22	73,59	113,14	152	78.500
ΣPAH	ND	ND	ND	132,28	589,93	706,06	1684	ND
ΣPAH / % TOC	ND	ND	ND	11,1	855	692,2	ND	ND

MW = Molecular Weight

*Quantification limit: EPA 8270D-1998

ND = Not defined

Table 3 summarizes the results of the physical and chemical characterization of the s&s samples. Higher TOC contents were observed in sediment than in the soil samples, which is consistent with the surrounding environment of shallow water surrounded by vegetation and mangroves, in comparison to the soil sample from industrial area where the presence of concrete structures predominated, that was later transformed to gardens with low coverage of trees.

The particle size distributions of the s&s samples show that predominant fractions are silts and sands followed by clays. The predominant particle size in the soils samples is 84µm, and in the sediment, 76µm. It is expected that clay particles contribute most to the specific surface area in the samples

The surface areas and pore volumes of the s&s samples are presented in table 3, and figures 1 and 2 show the accumulated distributions of surface areas as a function of pore diameters. It is observed that both soil samples have similar surface areas and pore volume distributions. Also, soil samples have relatively high surface areas and pore volumes while the sediment sample has lower surface area and pore volume.

Table 3. Chemical and physical characterization of soil and sediment samples.

Parameter	Unit	Sed 1	Sed 2	Soil 1	Soil 2
TOC	%	11,8 ±0,5	8,7 ±0,6	0,7 ±0,4	1,0 ±0,2
Sand	%	22	35	22	23

Silt	%	61	59	58	61
Clay	%	17	6	20	16
Surface area (BET*)	m ² /g	5,86	20,00	49,45	57,15
Surface area (DFT**)	m ² /g	4,53	18,29	38,95	48,20
Pore volume (DFT)	cc/g	0,02	0,03	0,07	0,07
ΣPAH	µg/kg	132,3	ND	589,9	706,1

*BET (Brunauer, Emmett and Teller model) [2].

**DFT (Density Functional Theory model) [2].

Analyzing the surface areas of the low-TOC soil samples it was found that at higher concentration of TOC the surface area is higher, because TOC offers additional surface area. However, in high-TOC sediment samples, the surface area is higher when the TOC is lower. This may be explained by increased obstruction of micropores at high TOC [16].

Likewise, the PAH content was directly affected by the available surface area in the soil samples because once adsorbed the PAH remain adsorbed.

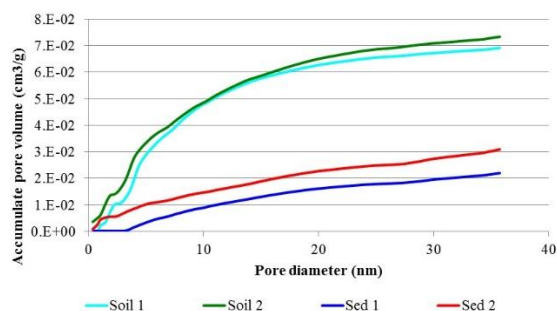


Fig. 1 Pore volume distribution in sediment and soil samples.

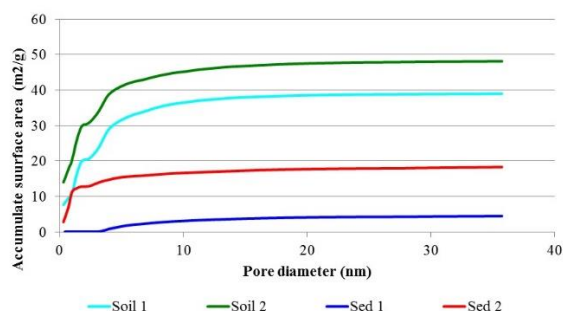


Fig. 2 Surface area distribution in sediment and soil samples.

The results of relating the contents of PAHs with solubility (K_{ow}) of these are observed in figure 3. No relationship was found between the concentrations of the PAH present in the different samples and their K_{ow} therefore the presence of these contaminants cannot be only attributed to its hydrophobicity. It can therefore be concluded that the PAH contents in the samples is more related to the characteristics of the porous medium than the physical and chemical properties of hydrocarbon.

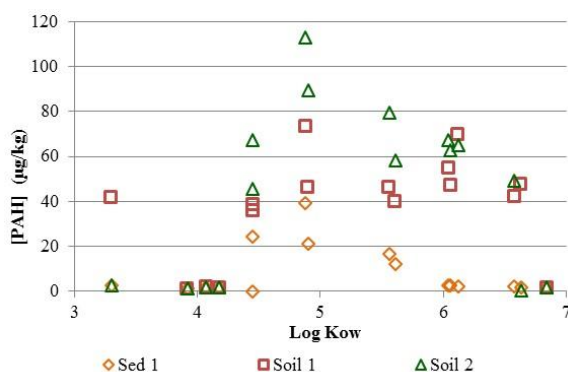


Fig. 3 Relation between concentrations of PAH in the samples and their K_{ow}

CONCLUSIONS

According to the results, the surface area of the porous medium is directly related to the concentration of PAH that can be retained in the medium.

The total organic carbon of the porous medium is a chemical characteristic that relates with the adsorption capacity of PAH; this relation seems to be direct for lower TOC and indirect for higher TOC, due to their contributions to the surface areas.

No direct relation was observed between K_{ow} and the concentrations of PAH in the sediment and soil samples.

Therefore, to plan effective remediation activities of contaminated sites, it is of prime importance to evaluate the characteristics of the porous media.

ACKNOWLEDGEMENTS

This paper is part of a project financed by the Mexican National Council of Science and Technology (Conacyt grant no. 241877). Adriana Villa Navia and Gonzalo Jayme Torres acknowledge the economic supports received from Conacyt. The authors wish to thank Axel Falcón Rojas for his support in the laboratory, and Stacey Alpuche for her review of the translation of the manuscript.

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