**SUPPLEMENTARY INFORMATION (SI)**

# Influence of natural organic matter fractions on PAH sorption by stream sediments and a synthetic graphene wool adsorbent

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## ADSORPTION MODELS

Kinetic experimental data was fitted to pseudo-first-order (eq. 1) and pseudo-second-order (eq. 2) kinetic models following the equations below:

$$q_t = q_e(1 - e^{-k_1 t}) \qquad (1)$$

$$q_t = \frac{q_e^2 k_2 t}{1 + k_2 q_e t} \qquad (2)$$

Where: $q_t$ and $q_e$ are the amount of solute sorbed per mass of sorbent (µg $g^{-1}$) at any time ($t$) and equilibrium, respectively; $k_1$ ($min^{-1}$) and $k_2$ (g $\mu g^{-1}$ $min^{-1}$) are rate constants for first-order and second-order adsorption (Lagergren, 1898; Kowanga et al., 2016). The initial sorption rate $(h)$ is defined by equation 3 (Kalavathy et al., 2005).

$$h = k_2 q_e^2 \qquad (3)$$

Furthermore, this study employed three different isotherm models viz: Freundlich (eq. 4), Langmuir (eq.5) and linear (eq.6), to fit the adsorption experimental data and Sum of Square Error (SSE) (eq.7) for validation;

$$q_e = K_f C_e^N \qquad (4)$$

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \qquad (5)$$

$$q_e = K_d C_e \qquad (6)$$

$$\sum_{i=1}^{n} (q_{e,cal} - q_{e,exp})_i^2 \qquad (7)$$

where $K_f$ (μg/g) (L/μg)$^N$) and $N$ (dimensionless) is Freundlich constant and intensity parameter, an indicator of site energy heterogeneity (He et al., 2006); $q_{max}$ (μg/g) and $K_L$ (L/μg) is the Langmuir maximum adsorption capacity and Langmuir constant associated with solute–surface interaction energy, respectively; $q_e$ is the solid-phase concentration (μg/g), $C_e$ is the liquid phase equilibrium concentration (μg/L), $K_d$ (L/g) is the sorption distribution coefficient, respectively.

The $K_d$ is a valuable parameter in the evaluation of organic pollutants partitioning in the water environment. The $K_d$ was used to estimate the single point organic carbon-normalized distribution coefficients, $K_{oc}$ according to the following:

$$K_{oc} = K_d / f_{oc} \approx q_e / (C_e . f_{oc}) \qquad (8)$$

where $f_{oc}$ is the fraction of organic carbon (Ololade et al., 2018).

## FIGURES

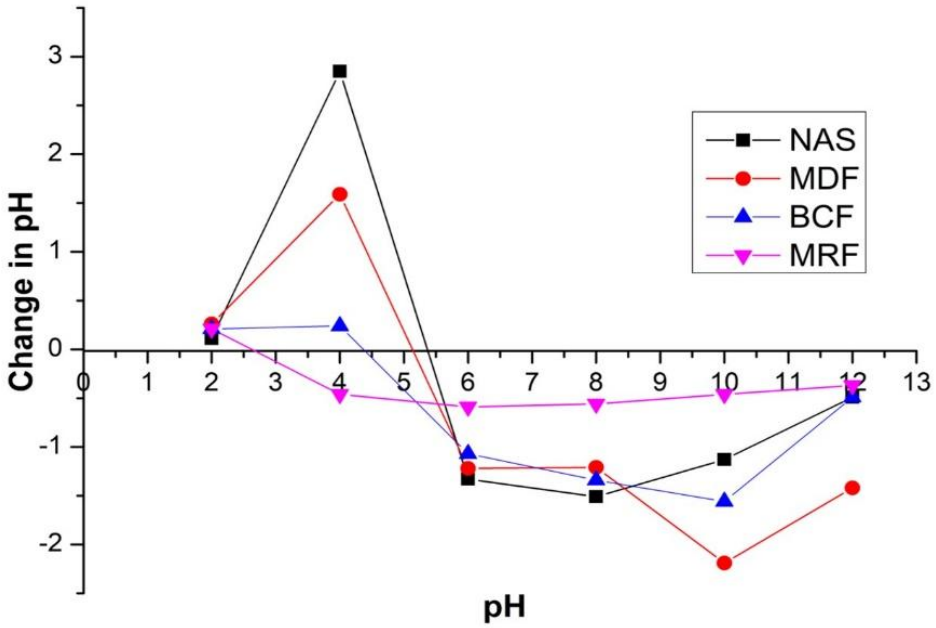


**Figure S1:** Point of zero net charge of sediment and its components

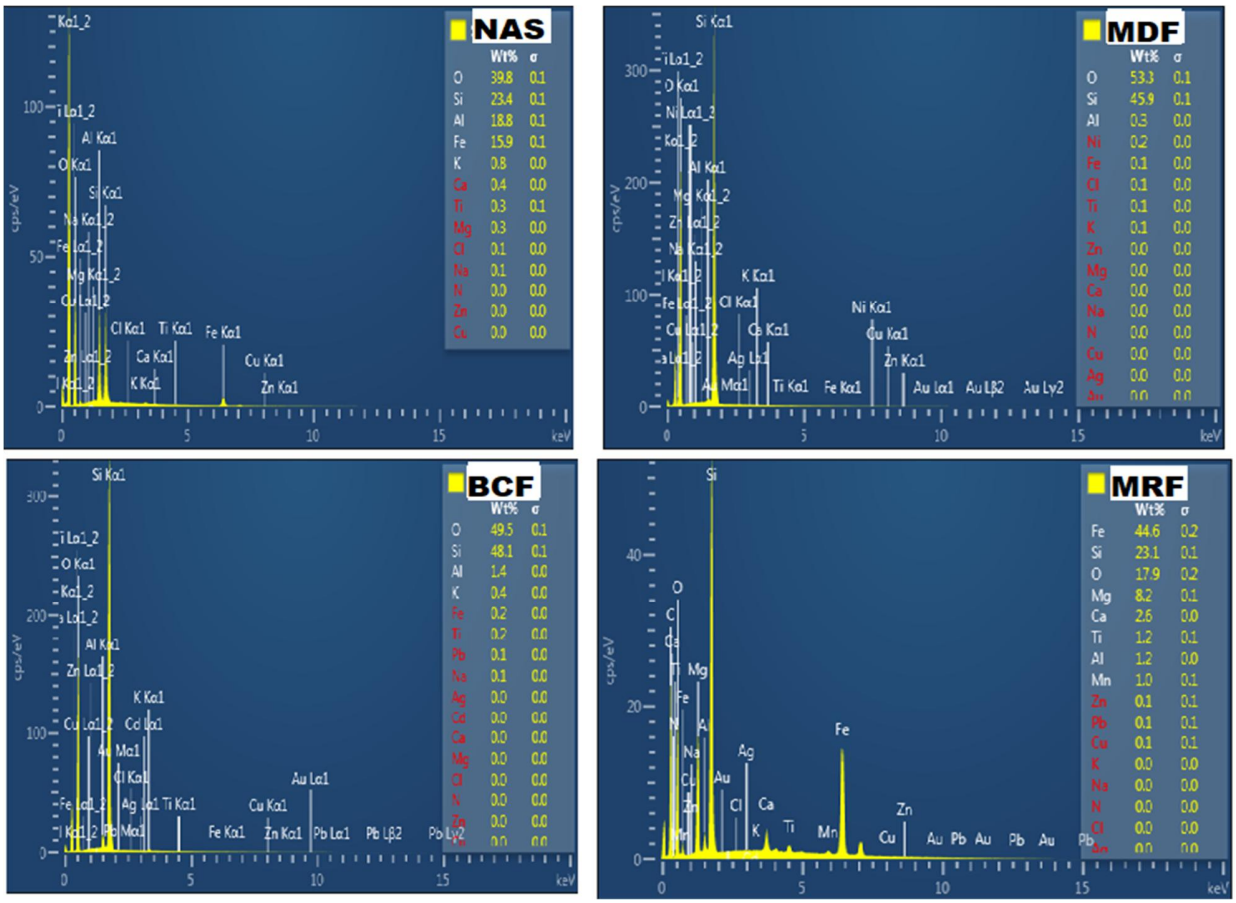


**Figure S2:** Results of EDS analysis of natural sediment and its components

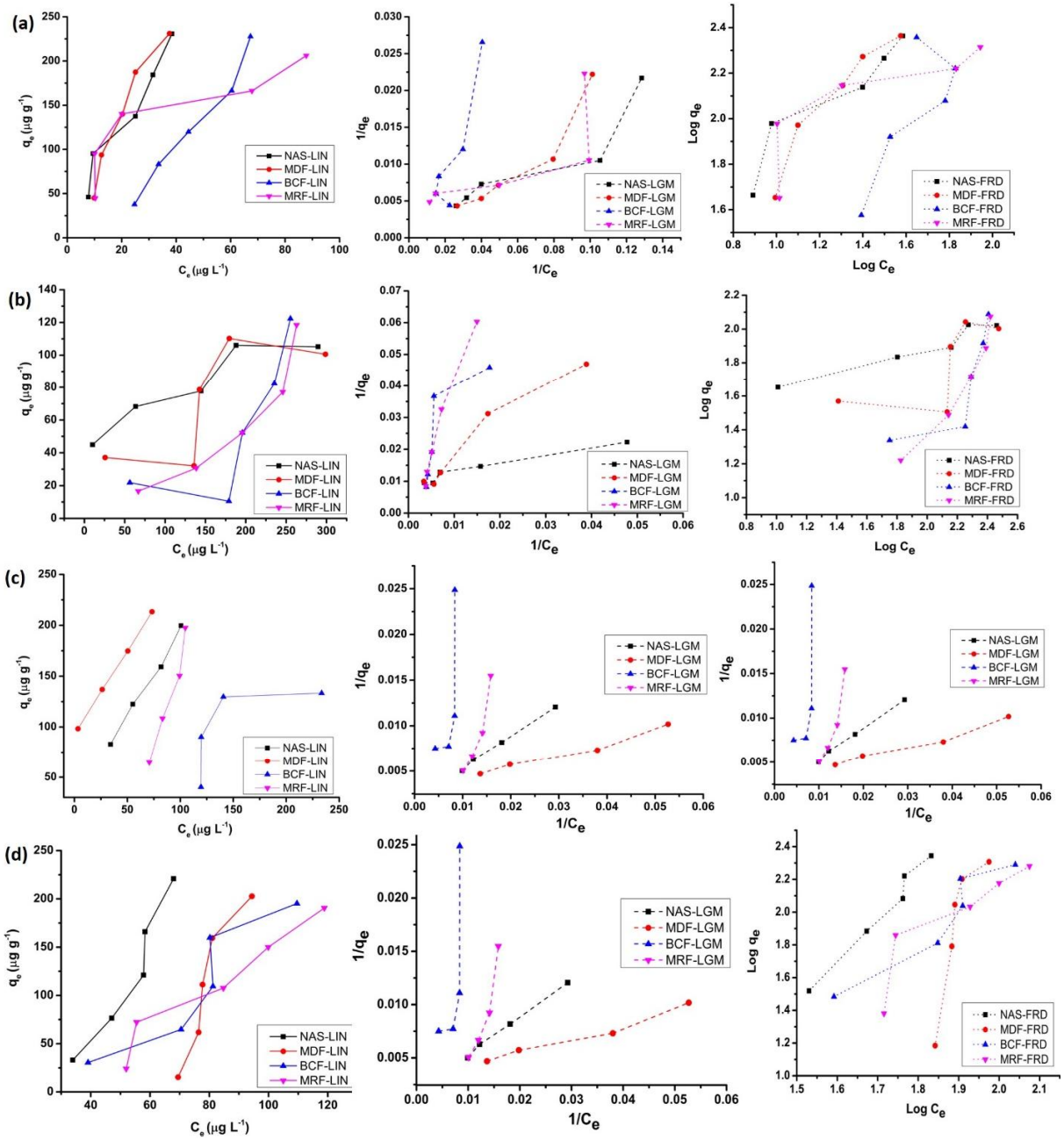


**Figure S3:** Linear equation isotherm plots for Linear (LIN), Langmuir (LGM), and Freundlich (FRD) sorption models, (a) Naphthalene (b) Phenanthrene (c) Pyrene (d) Perylene, onto natural sediment (NAS), mineral-deficient fraction (MDF), black carbon fraction (BCF) and mineral-rich fraction (MRF).

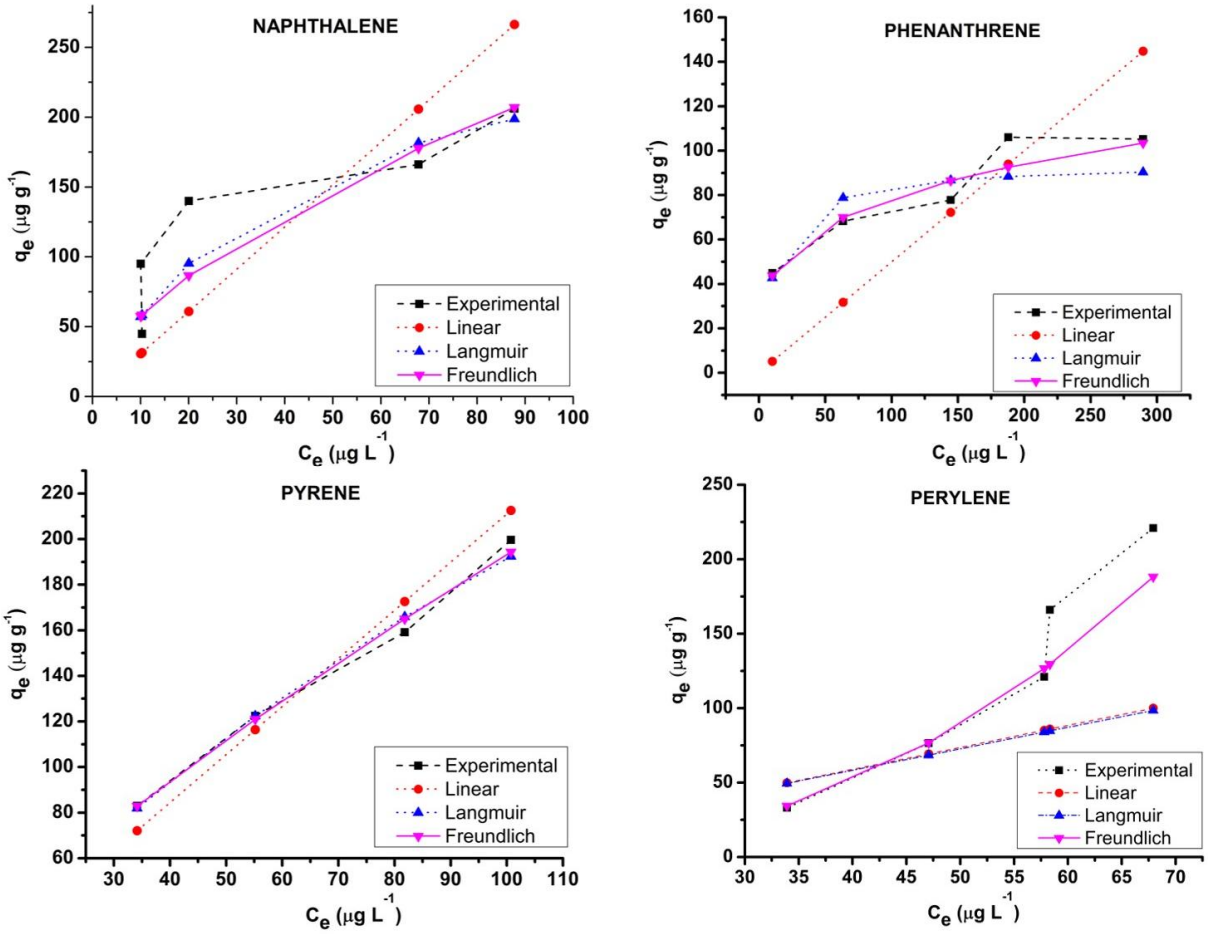


**Figure S4**: Representative nonlinear equation isotherm model plots for adsorption of selected PAHs onto natural sediments and validated by Error Sum of Squares (SSE).

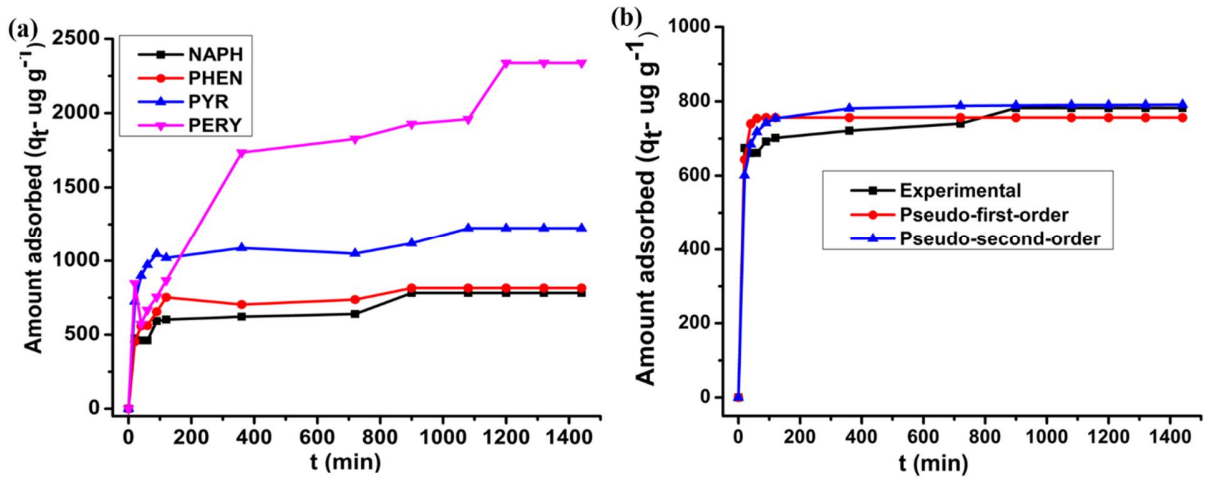


**Figure S5:** (a) Time-concentration profile of adsorption of NAPH, PHEN, PYR, and PERY onto natural sediment (b) Fitting pseudo-first (PFO) and second (PSO) order kinetic models to adsorption of NAPH on natural sediment {Error Sum of Squared (SSE) are 0.13 (PFO) and 0.08 (PSO)}.

## TABLES

**Table S1:** Physicochemical properties of selected polycyclic aromatic hydrocarbons

| PAHs | Molecular formula | [a]Log*Kow* | [c]Sw (mg $L^{-1}$) | [a]Mw (g $mol^{-1}$) | [b]Bp (˚C) |
|---|---|---|---|---|---|
| **Naphthalene** | $C_{10}H_8$ | 3.30 | 31.0 | 128.2 | 217.9 |
| **Phenanthrene** | $C_{14}H_{10}$ | 4.46 | 1.18 | 178.2 | 340.0 |
| **Pyrene** | $C_{16}H_{10}$ | 5.13 | 0.135 | 202.3 | 404.0 |
| **Perylene** | $C_{22}H_{12}$ | 6.30 | 4e-4 | 252.3 | 467.0 |

*Log $K_{ow}$:octanol-water partition coefficient, $S_w$: water solubility (mg $L^{-1}$), $M_w$: molecular weight (g $cmol^{-1}$), $B_p$: boiling points ($^oC$). Cited from [a](Sun et al., 2013), [b](Yakout and Daifullah, 2013), [c](Potin et al., 2004).*

**Table S2:** ICP-OES elemental analysis of concentration (ppm ± std) major elements present in natural and fractions of stream sediment

| Elements | Natural Sediment (NAS) | Mineral Deficient Fraction (MDF) | Black Carbon Fraction (BCF) | Mineral Rich Fraction (MRF) |
|---|---|---|---|---|
| Aluminum (Al) | 218.55 ± 0.61 | 9.29 ± 0.37 | 3.105 ± 0.05 | 65.50 ± 0.20 |
| Iron (Fe) | 692.20 ± 0.60 | 12.67 ± 0.02 | 1.63 ± 0.02 | 298.90 ± 0.69 |
| Phosphorus (P) | 16.17 ± 0.07 | 2.48 ± 0.07 | 1.03 ± 0.15 | 15.69 ± 0.24 |
| Silicon (Si) | 28.34 ± 0.58 | 3.49 ± 0.97 | 1.68 ± 0.17 | 18.43 ± 0.24 |
| Manganese (Mn) | 14.92 ± 0.21 | 0.06 ± 0.0 | 0.03 ± 0.001 | 1.84 ± 0.02 |
| Lead (Pb) | 0.71 ± 0.10 | < 0.09 ± 0.01 | < 0.14 ± 0.014 | 0.31 ± 0.04 |
| Sodium (Na) | 10.54 ± 0.17 | 2.01 ± 0.05 | 1.42 ± 0.07 | 7.01 ± 0.10 |
| Potassium (K) | 6.94 ± 0.08 | 4.81 ± 0.10 | 4.23 ± 0.06 | 5.58 ± 0.11 |
| Calcium (Ca) | 31.74 ± 0.09 | 2.64 ± 0.05 | 1.60 ± 0.02 | 8.26 ± 0.05 |
| Magnesium (Mg) | 16.54 ± 0.15 | 0.65 ± 0.01 | 0.30 ± 0.002 | 6.76 ± 0.01 |

**Table S3:** Sorption model parameters for adsorption of NAPH onto natural sediments and its components

| Sorption models | Parameters | NAS | MDF | BCF | MRF |
|---|---|---|---|---|---|
| | $K_f$ | 8.46 | 3.48 | 0.63 | 14.71 |
| **Freundlich** | $N$ | 0.89 | 1.19 | 1.32 | 0.59 |
| | $SSE$ | 0.14 | 0.14 | 0.44 | 0.40 |
| **Langmuir** | $q_{max}\ (\mu g\ g^{-1})$ | 1049 | 10678 | 13212 | 293 |
| | $K_L\ (L\ \mu g^{-1})$ | 0.007 | 0.001 | 0.0002 | 0.02 |
| | $SSE$ | 0.15 | 0.20 | 0.54 | 0.36 |
| **Linear** | $K_d$ | 6.13 | 6.05 | 2.07 | 3.03 |
| | $SSE$ | 0.17 | 0.19 | 0.54 | 1.01 |
| | $LogK_{oc}$ | 1.95 | 1.81 | 1.32 | 1.93 |

**Table S4**: Sorption model parameters for adsorption of PHEN onto natural sediments and its components

| Sorption models | Parameters | NAS | MDF | BCF | MRF |
|---|---|---|---|---|---|
| | $K_f$ | 24.10 | 10.88 | 12.36 | 0.06 |
| **Freundlich** | $N$ | 0.26 | 0.31 | 0.04 | 1.31 |
| | $SSE$ | 0.03 | 0.87 | 2.24 | 1.15 |
| **Langmuir** | $q_{max}\,(\mu g\ g^{-1})$ | 94 | 55 | 240 | 235 |
| | $K_L\,(L\ \mu g^{-1})$ | 0.08 | 0.07 | 15.30 | 0.001 |
| | $SSE$ | 0.09 | 0.96 | 2.23 | 0.25 |
| **Linear** | $K_d$ | 0.50 | 0.34 | 0.09 | 0.27 |
| | $SSE$ | 1.23 | 1.12 | 2.53 | 0.23 |
| | $LogK_{oc}$ | 0.87 | 0.56 | 0.04 | 0.60 |

**Table S5:** Sorption model parameters for adsorption of PYR onto natural sediments and its components

| Sorption models | Parameters | NAS | MDF | BCF | MRF |
|---|---|---|---|---|---|
| | $K_f$ | 5.13 | 70.60 | 0.05 | 1.0e-3 |
| **Freundlich** | $N$ | 0.79 | 0.23 | 1.46 | 0.38 |
| | $SSE$ | 0.002 | 0.023 | 0.510 | 0.014 |
| **Langmuir** | $q_{max}\,(\mu g\ g^{-1})$ | 624 | 180 | 3402 | 6216 |
| | $K_L\,(L\ \mu g^{-1})$ | 4e-3 | 3e-1 | 1e-4 | 2e-4 |
| | $SSE$ | 0.003 | 0.069 | 0.57 | 0.29 |
| **Linear** | $K_d$ | 2.11 | 3.59 | 0.48 | 1.21 |
| | $SSE$ | 0.03 | 0.92 | 0.57 | 0.28 |
| | $LogK_{oc}$ | 0.85 | 1.58 | 0.58 | 1.26 |

**Table S6:** Sorption model parameters for adsorption of PERY onto natural sediments and its components

| Sorption models | Parameters | NAS | MDF | BCF | MRF |
|---|---|---|---|---|---|
| | $K_f$ | 6.2e-3 | 9.4e-6 | 3.1e-2 | 2.4e-3 |
| **Freundlich** | $N$ | 2.45 | 3.46 | 1.85 | 2.39 |
| | $SSE$ | 0.19 | 2.01 | 0.20 | 0.36 |
| **Langmuir** | $q_{max}\,(\mu g\ g^{-1})$ | 7853 | 1521 | 6960 | 5807 |
| | $K_L\,(L\ \mu g^{-1})$ | 1.9e-4 | 2.2e-4 | 1.5e-4 | 1.3e-4 |
| | $SSE$ | 0.90 | 2.60 | 0.59 | 1.28 |
| **Linear** | $K_d$ | 1.47 | 0.32 | 1.06 | 0.75 |
| | $SSE$ | 0.89 | 2.60 | 0.58 | 1.27 |
| | $LogK_{oc}$ | 1.34 | 0.53 | 1.03 | 1.04 |

**Table S7:** Thermodynamic parameters for the adsorption of naphthalene (NAPH), phenanthrene (PHEN), pyrene (PYR) and perylene (PERY) onto sediment components

| PAH | Temp. (K) | NAS | | | MDF | | | BCF | | | MRF | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | ΔG ($J\ mol^{-1}K^{-1}$) | ΔH ($J\ mol^{-1}$) | ΔS ($J\ mol^{-1}$) | ΔG ($Jmol^{-1}K^{-1}$) | ΔH ($J\ mol^{-1}$) | ΔS ($k\ Jmol^{-1}$) | ΔG ($J\ mol^{-1}K^{-1}$) | ΔH ($J\ mol^{-1}$) | ΔS ($J\ mol^{-1}$) | ΔG ($J\ mol^{-1}K^{-1}$) | ΔH ($J\ mol^{-1}$) | ΔS ($J\ mol^{-1}$) |
| **NAPH** | 298 | -37.7 | | | -80.2 | | | -45.9 | | | -19.9 | | |
| | 308 | -86.2 | 1207.4 | 4.2 | -125.2 | 1260.8 | 4.5 | -99.1 | 1502.5 | 5.2 | -57.9 | 1112.5 | 3.8 |
| | 318 | -128.2 | | | -170.2 | | | -151.1 | | | -95.9 | | |
| **PHEN** | 298 | 56.9 | | | 5.2 | | | 40.5 | | | 20.9 | | |
| | 308 | -5.1 | 1904.5 | 6.2 | -11.2 | 2298.8 | 7.5 | 6.6 | 1269.4 | 4.1 | -10.4 | 925.9 | 3.0 |
| | 318 | -67.1 | | | -86.2 | | | -34.4 | | | -28.1 | | |
| **PYR** | 298 | -13.2 | | | -15.4 | | | -28.8 | | | -25.1 | | |
| | 308 | 14.4 | -1186.8 | -3.9 | 32.5 | -1661.5 | -5.5 | 2.2 | -952.6 | -3.1 | 14.9 | -1217.1 | -4.0 |
| | 318 | 53.3 | | | 87.5 | | | 33.2 | | | 54.9 | | |
| PERY | 298 | -41.8 | | | -113.4 | | | -34.1 | | | -71.4 | | |
| | 308 | -33.8 | -280.2 | -0.8 | -59.4 | -1722.6 | -5.4 | -1.1 | -1017.5 | -3.3 | -10.8 | -2453.2 | -8.0 |
| | 318 | -25.8 | | | -5.4 | | | 31.9 | | | 90.8 | | |

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