THE ENVIRONMENTAL IMPACT OF POLYCYCLIC AROMATIC HYDROCARBONS IN THE SEDIMENT RIVER

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SUPERVISOR'S DECLARATION

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I hereby declare that the work in this thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at Universiti Malaysia Pahang or any other institutions.

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LIST OF SYMBOLS

mg	milligram
g	gram
nm	nano metre
µm	micro metre
ml	mililitre
min^{-1}	per minute
mg/m^3	miligram per cubic metre
ng/m^3	nanogram per cubic metre
l/mg	litre per milligram
ng/g	nanogram per gram
µg/g	microgram per gram
kg/l	kilogram per litre
mg/l	miligram per litre
µg/L	microgram per litre
ng/L	nano gram per litre
g/mol	gram per mol
$m^{3/}$mol	cubic metre per mol
mol/L	mol per litre
ml/min	miligram per minute
°C	degree celcius
%	percent
h	hour
K	Kelvin

Pa	Pascal
rpm	revolution per minute
M	molarity
ppt	part per thousand
ppb	part per billion
mPa	mega Pascal
mm Hg	milimeter of mercury
K_{ow}	octanol-water partition coefficient
K_p	partition coefficient
K_f	Freundlich sorption coefficient
K_L	Langmuir sorption coefficient
K_d	Linear sorption coefficient

LIST OF ABBREVIATIONS

PAHs	Polycyclic Aromatic Hydrocarbons
POPs	Persistent Organic Pollutants
USEPA	United State Environmental Protection Agency
CCME	Canadian Council of Ministers of the Environments
CEPA	Canadian Environmental Protection Act
ATSDR	Agency for Toxic Substances and Disease Registry
ASTM	American Society for Testing and Materials
OECD	Organisation for Economic Co-operation and Development
ACGIH	American Conference of Governmental Industrial Hygienists
NIOSH	National Institute for Occupational Safety and Health
OSHA	Occupational Safety and Health Administration
EPA	Environmental Protection Act
WHO	World Health Organisation
EPISUITE	Estimation Program Interface
RP-HPLC	Reverse Phase high Performance Liquid Chromatography
LMW	Low Molecular Weight
HMW	High Molecular Weight
EFMs	Environmental Fate Models
QSAR	Quantitative structure-activity relationship
SPE	Solid Phase Extraction
LOD	Limit of Detection
PHE/ANT	Phenanthrene/anthracene
FL/PYR	Fluoranthene/pyrene

B[a]A/CHR	Benz[a]anthracene/chrysene
B[b]FA	Benzo[b]fluoranthene/benzo[k]fluoranthene
B[a]PYR/ B[ghi]PER	Benzo[a]pyrene/benzo[g,h,i]perylene
ACN	Acenaphtylene
PHE	Phenanthrene
FL	Fluorene
PY	Pyrene
CHR	Chrysene
PER	Perylene
B[a]A	Benzo[a]anthracene
B[a]P	Benzo[a]pyrene
B[b]F	Benzo[b]fluoranthene
B[ghi]P	Benzo[ghi]pyrene
B[b]FL)	Benzo[b]fluoranthene
B[k]FL	Benzo[k]fluorenthene
B[ghi]FL	Benzo[ghi]fluorenthene
KCl	Sodium chloride
HCl	Acid hydrochloric
NaOH	Natrium hydroxide

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ABSTRAK

Polisiklik Aromatik Hidrokarbon (PAH) adalah bahan yang berterusan ada dalam alam sekitar dan menjadi kebimbangan kerana ketoksikan dan mutagen bahan ini. Kehadiran PAH di Malaysia telah dilaporkan, dengan itu kajian ini dijalankan untuk menilai lagi kesan bahan ini kepada alam sekitar terutama dalam sedimen sungai dengan menentukan sifat PAHs dan faktor-faktor yang mengawalnya. Penyelidikan ini bermula dengan penyiasatan kapasiti penyerapan atau kemampuan PAHs ini dalam sedimen dan hubungan antara serapan dan pekali pembahagian oktanol-air mereka (K_{ow}). Pekali partition oktanol-air (K_{ow}) adalah peramal yang baik bagi serapan antara pencemar setelah keputusan menunjukkan bahawa pepejal air partition pekali (K_{oc}) meningkat apabila pekali partition oktanol-air (K_{ow}) meningkat. Data serapan telah digunakan bagi melakar graf Linear, Freundlich dan Langmuir model isoterma dan pekali linear regresi (R^2) untuk Freundlich isoterma adalah yang tertinggi (>0.98) di antara tiga model ini. Oleh itu, tingkah laku sorption yang PAH dalam sedimen sungai adalah' physisorption' kerana ia patuh kepada model isoterma Freundlich. Kesan yang ketara ke atas PAH sifat telah diperhatikan dalam sedimen disebabkan oleh perubahan kemasinan, pH dan suhu yang ditunjukkan oleh pekali kapasiti penyerapan (K_f) yang diperolehi daripada eksperimen. Pekali kapasiti penyerapan (K_f) meningkat apabila kemasinan meningkat tetapi sebaliknya apabila pH dan suhu meningkat. 'pseudo-first order', 'pseudo-second order', 'Elovichs' equation' and 'fractional power' model telah di lakar dan 'pseudo-second order' di pilih mewakili penjerapan mekanisme kinetik kerana ia mempunyai pekali yang paling tinggi linear regresi (R^2> 0.99). 'Pseudo-second order' mengesahkan bahawa kehadiran liang dalam sistem sedimen adalah faktor pengehad kepada mekanisme kadar penjerapan. Selain itu, tiga kaedah yang berbeza digunakan bagi pengekstrakan fasa pepejal untuk meningkatkan kepekatan sampel dan kaedah dari Supelco menunjukkan peratusan pemulihan tertinggi (73.53% kepada 88,29%) berbanding kaedah lain. Akhir sekali, hasil kajian ini juga menunjukkan perbezaan yang besar antara nilai-nilai eksperimen dan nilai-nilai yang dihasilkan oleh model pengiraan iaitu 'Estimation Program Interface' (EPISUITE). Oleh itu, kajian ini menunjukkan bahawa walaupun model pengiraan boleh digunakan tetapi ia tidak tepat menilai kesan alam sekitar daripada bahan pencemar. Eksperimen tetap perlu dilakukan untuk mendapatkan pembahagian sebenar PAH di dalam alam sekitar.

ABSTRACT

Polycyclic Aromatic Hydrocarbons (PAHs) are ubiquitous in the environment and amongst greatest concern due to their toxicity and mutagenicity. As the occurrences of PAHs in Malaysia have been reported, thus this study was conducted to further assess their environmental impact in river sediments by determination of PAHs behavior and factors that govern it. The research started with the investigation of the sorption capacity or affinity of these PAHs in sediments and the relationship between sorption and their octanol-water partition coefficient (K_{ow}). The octanol-water partition coefficient (K_{ow}) was a good predictor of sorption among pollutant as the results show that the solid-water partition coefficient (K_{oc}) increased as the octanol-water partition coefficient (K_{ow}) increased. The sorption data was plotted to graphs Linear, Freundlich and Langmuir isotherm model and the linear regression coefficient (R^2) obtained for Freundlich isotherm was the highest (>0.98) among these three models. Thus, the sorption behavior of PAHs in river sediments was physisorption as it obeyed the Freundlich isotherm model. A significant effect on PAHs behavioral was observed in sediments caused by changes of salinity, pH and temperature which was indicated by the sorption capacity coefficient (K_f) obtained from batch sorption equilibrium experiments. The sorption capacity coefficient (K_f) increased as the salinity increased but vice versa as the pH and temperature was increased. The pseudo-first order, pseudo-second order, Elovichs' equation and fractional power model graphs was plotted and pseudo-second order represents the adsorption kinetic mechanism since it has the highest linear regression coefficient (R^2>0.99). Pseudo-second order confirmed that presence of pores in the sediments system was the limiting factor to the adsorption rate mechanism. Besides that, three different method of solid phase extraction were applied to pre-concentrate the samples and the method from Supelco show the highest percentage of recovery (73.53% to 88.29%) compared to other method from previous literature. Finally, the results of this study also indicated a considerable difference between experimental values and values generated by the computational model, Estimation Program Interface (EPISUITE). Thus, this study strongly shows that although the computational model was indicative, it does not accurately assess the environmental impact of pollutant. The experiments need to be conducted to obtain the real partitioning of PAHs in environment.

REFERENCES

Abdel-Shafy, H. I., & Mansour, M. S. M. (2015). A review on polycyclic aromatic hydrocarbons: Source, environmental impact, effect on human health and remediation. *Egyptian Journal of Petroleum*, *25*(1), 107–123. doi:10.1016/j.jpe. 2015.03.011

Ahangar, A. G. (2010). Sorption of PAHs in the soil environment with emphasis on the role of soil organic matter : a review. *World Applied Sciences Journal, 11*(7), 759–765.

ASTM D2974. (2000). Standard test methods for moisture, ash and organic matter of peat and other organic soils.

ASTM E1195. (2001). Standard test method for determining a sorption constant (K_{oc}) for an organic chemical in soil and sediments.

ATSDR (Agency for Toxic Substances and Disease Registry), U.S. Department of Health and Human Services, Public Health Service. (1995). Toxicological Profile for Polycyclic Aromatic Hydrocarbons. Retrieved from http://www.atsdr.cdc.gov/toxprofiles/tp.asp?id=122&tid=25

Awoyemi, A. (2011). Understanding the adsorption of polycyclic aromatic hydrocarbons from aqeous phase onto activated carbon (Master's thesis). ISBN: 9780494764244 0494764244

Azhari, A., Dalimin, M. N., & Wee, S. T. (2011). Polycyclic aromatic hydrocarbons (PAHs) from vehicle emission in the vegetation of highway roadside in Johor, Malaysia. *International Journal of Environmental Science and Development, 2*(6), 465–468.

Azizian, S. (2004). Kinetic models of sorption: A theoretical analysis. *Journal of Colloid and Interface Science, 276*, 47–52. doi:10.1016/j.jcis.2004.03.048

Bakhtiari, A. R., Zakaria, M. P., Yaziz, M. I., Lajis, M. N. H., & Bi, X. (2011). Polycyclic aromatic hydrocarbons and n-alkanes in suspended particulate matter and sediemnts from the Langat River, Peninsular Malaysia. *Thai Society of Higher Education Institutes on Environment, 2*, 1-10.

Barra, R., Quiroz, R., Saez, K., Araneda, A., Urrutia, R., & Popp, P. (2008). Sources of polycyclic aromatic hydrocarbons (PAHs) in sediments of the Biobio River in south central Chile. *Environmental Chemistry Letters, 7*, 133–139. doi: 10.1007/s10311-008-0148-z

Bisht, S., Pandey, P., Bhargava, B., Sharma, S., Kumar, V., & Krishan, D. (2015). Bioremediation of polyaromatic hydrocarbons (PAHs) using rhizosphere technology. *Brazilian Journal of Microbiology, 46*(1), 7–21. doi: 10.1590/S1517-838246120131354

Boonyatumanond, R., Wattayakorn, G., Togo, A., & Takada, H. (2006). Distribution and origins of polycyclic aromatic hydrocarbons (PAHs) in riverine, estuarine, and marine sediments in Thailand. *Marine Pollution Bulletin*, *52*, 942–956. doi: 10.1016/j.marpolbul.2005.12.015

CCME. Canadian soil quality guidelines for carcinogenic and other polycyclic aromatic hydrocarbons (PAHs) (Environmental and human health effects). (2010). Canadian Council of Ministers of the Environment. PN 1445, ISBN 978-1-896997-94-0 PDF

CEPA. Priority substance list assessment report, polycyclic aromatic hydrocarbons. (1994). Canadian Environmental Protection Act. ISBN 0-662-22209-1

Chen, Y., Jia, R., & Yang, S. (2015). Distribution and source of polycyclic aromatic hydrocarbons (PAHs) in water dissolved phase, suspended particulate matter and sediment from Weihe River in Northwest China. *International Journal of Environmental Research and Public Health*, *12* (11), 14148–14163. doi: 10.3390/ijerph121114148

Ciesielczuk, T., Kusza, G., Poluszyńska, J., & Kochanowska, K. (2014). Pollution of flooded arable soils with heavy metals and polycyclic aromatic hydrocarbons (PAHs). *Water, Air, & Soil Pollution, 225,* 2145. doi: 10.1007/s11270-014-2145-0

De Luca, G., Furesi, A., Leardi, R., Micera, G., Panzanelli, A., Costantina Piu, P., & Sanna, G. (2004). Polycyclic aromatic hydrocarbons assessment in the sediments of the Porto Torres Harbor (Northern Sardinia, Italy). *Marine Chemistry*, *86*, 15–32. doi: 10.1016/j.marchem.2003.11.001

Delle, A. (2001). Factors affecting sorption of organic compounds in natural sorbent õ water systems and sorption coefficients for selected pollutants: a review. *Journal of Physical Chemical Reference Data, 30*(1). doi: 10.1063/1.1347984

Eisler, R. (1987). Polycyclic aromatic hydrocarbon hazards to fish, wildlife, and invertebrates: a synoptic review. U.S. Fish and Wildlife Service Biological Report 85(1.6). 60 pp). Laurel, MD: Patuxent Wildlife Research Center.

Elias, S., Wood, A. K., Hashim, Z., Siong, W. B., Hamzah, M. S., Rahman, A., Salim, N. A. A., & Talib, A. (2007). Polycyclic aromatic hydrocarbon (PAH) contamination in the sediments of East Coast of Peninsular Malaysia. *The Malaysian Journal of Analytical Science*, *11*(1), 70–75.

Fernandes, M. B., Sicre, M., Boireau, A., & Tronczynski, J. (1997). Polyaromatic hydrocarbon (PAH) distributions in the Seine River and its estuary. *Marine Pollution Bulletin, 34*(11), 857–867.

Foo, K. Y., & Hameed, B. H. (2010). Insights into the modeling of adsorption isotherm systems. *Chemical Engineering Journal*, *156*, 2–10. doi:10.1016/j.cej.2009.09.013

Frapiccini, E., & Marini, M. (2015). Polycyclic aromatic hydrocarbon degradation and sorption parameters in coastal and open-sea sediment. *Water Air Soil Pollution*, 226: 246. doi:10.1007/s11270-015-2510-7.

Gilgenast, E., Boczkaj, G., Przyjazny, A., & Kamiński, M. (2011). Sample preparation procedure for the determination of polycyclic aromatic hydrocarbons in petroleum vacuum residue and bitumen. *Analytical and Bioanalytical Chemistry*, *401*, 1059–1069. doi: 10.1007/s00216-011-5134-9

Gschwend, P. M., & Wu, S. (1985). On the constancy of sediment-water partition coefficients of hydrophobic organic pollutants. *Environmental Science & Technology, 19*(1), 90–96. doi:10.1021/es00131a011

Gschwend, P.M., & Hites, R. A. (1981). Fluxes of polycyclic aromatic hydrocarbons to marine and lacustrine sediments in north eastern United State. *Geochimica et Cosmochimica Acta, 45*(12), 2359-2367. doi:10.1016/0016-7037(81)90089-2

Haftka, J. J. H., Govers, H. A. J., & Parsons, J. R. (2010). Influence of temperature and origin of dissolved organic matter on the partitioning behavior of polycyclic aromatic hydrocarbons. *Environmental Science and Pollution Research International*, *17*, 1070–1079. doi: 10.1007/s11356-009-0263-9

Havelcová, M., Melegy, A., & Rapant, S. (2014). Geochemical distribution of polycyclic aromatic hydrocarbons in soils and sediments of El-Tabbin, Egypt. *Chemosphere*, *95*, 63–74. doi: 10.1016/j.chemosphere.2013.08.018.

Heemken, O. P., Stachel, B., Theobald, N., & Wenclawiak, B. W. (2000). Environmental contamination and t oxicology temporal variability of organic micropollutants in suspended particulate matter of the River Elbe at Hamburg and the River Mulde at Dessau, Germany. *Archives of Environmental Contamination and Toxicology*, *38*, 11–31.

Hiller, E., Jurkovič, Ľ., & Bartaľ, M. (2008). Effect of temperature on the distribution of polycyclic aromatic hydrocarbons in soil and sediment. *Soil and Water Resources, 3*(4) 231–240.

Huang, Y., Wei, J., Song, J., Chen, M., & Luo, Y. (2013). Chemosphere determination of low levels of polycyclic aromatic hydrocarbons in soil by high performance liquid chromatography with tandem fluorescence and diode-array detectors. *Chemosphere*, *92*, 1010–1016. doi: 10.1016/j.chemosphere.2013.03.035.

Igwe, J. C. (2015). Environmental effects of polycyclic aromatic hydrocarbons. *Journal of Natural Science Research, 5*(7), 117–132.

Jones, K. C. K. C., & de Voogt, P. (1999). Persistent organic pollutants (POPs): state of the science. *Environmental Pollution*, *100*, 209–221. doi: 10.1016/S0269-7491(99)00098-6

Kafilzadeh, F., Shiva, A. H., & Malekpour, R. (2011). Determination of polycyclic aromatic hydrocarbons (PAHs) in water and sediments of the Kor River, Iran. *Middle-East Journal of Scientific Research, 10*(1), 1–7.

Kah, M., & Brown, C. D. (2008). Log D: Lipophilicity for ionisable compounds. *Chemosphere*, *72*, 1401–1408. doi: 10.1016/j.chemosphere.2008.04.074.

Kanchamayoon, W., & Tatrahun, N. (2009). Extraction of eleven polycyclic aromatic hydrocarbon in water samples. *Journal of Environmental Science and Technology, 2*(2), 95-99.

Keenan, A.Sakultantimetha, & Bangkhedpol, S. (2010). Envrionmental fate and aprtition coefficient of oestrogen compound in sewage treatment process. *Environmental Research, 106,* pp 313-318.

Keshavarzifard, M., Zakaria, M. P., Hwai, Yusuff, F. M., N., Mustafa, S., Vaezzadeh, V., Magam, S. M., Masood, N., Alkhadher, S. A. A., & Abootalebi-Jahromi, F. (2014). Baseline distributions and sources of polycyclic aromatic hydrocarbons (PAHs) in sediments from Prai and Malacca Rivers, Peninsular Malaysia. *Marine Pollution Bulletin, 88*, 366–372. doi: 10.1016/j.marpolbul.2014.08.014

Khodadoust, A. P., Lei, L., Antia, J. E., Bagchi, R., Suidan, M. T., & Tabak, H. H. (2005). Adsorption of polycyclic aromatic hydrocarbons in aged harbor sediments. *Journal of Environmental Engineering*, *131*(3), 403–409. doi: 10.1061/(ASCE)0733-9372(2005)131:3(403)

Kinniburgh, D. G. (1986). General purpose adsorption isotherms. *Environmental Science & Technology, 20*(9), 895–904. doi: 10.1021/es00151a008

Kishida, M., Imamura, K., Takenaka, N., Maeda, Y., Viet, P. H., & Bandow, H. (2008). Concentrations of atmospheric polycyclic aromatic hydrocarbons in particulate matter and the gaseous phase at roadside sites in Hanoi, Vietnam. *Bulletin of Environmental Contamination and Toxicology, 81,* 174–9. doi: 10.1007/s00128-008-9450-5

Kiss, G., Varga-Punchony, Z., Tolnai, B., Varga, B., Gelencser, A., Krivacsy, Z., & Hlavavy, J. (2001). The seasonal changes in the concentration of polycyclic aromatic hydrocarbons in precipitation and aerosol near Lake Balaton, Hungary. *Environmental Pollution*, *114*, 55-61. doi: 10.1016/s0269-7491(00)00208-6

Kuppithayanant, N., Rayanakorn, M., Wongpornchai, S., Prapamontol, T., & Deming, R. L. (2003). Enhanced sensitivity and selectivity in the detection of polycyclic aromatic hydrocarbons using sequential simplex optimization, the addition of an organic modifier and wavelength programming. *Talanta, 61,* 879–888. doi: 10.1016/S0039-9140(03)00374-6

Liu, F., Liu, J., Chen, Q., Wang, B., & Cao, Z. (2012). Pollution characteristics, ecological risk and sources of polycyclic aromatic hydrocarbons (PAHs) in surface sediment from Tuhai-Majia River system, China. *Procedia Environmental Sciences*, *13*, 1301–1314. doi: 10.1016/j.proenv.2012.01.123

Liu, Y., Liu, L., Lin, J., Tang, N., & Hayakawa, K. (2006). Distribution and characterization of polyclic aromatic hydrocarbons compounds in airborne particulated of East Asia, *China Particuology, 4*(6), 283–292.

Lohmann, R., Breivik, K., Dachs, J., & Muir, D. (2007). Global fate of POPs: Current and future research directions. *Environmental Pollution*, *150*, 150–165. doi: 10.1016/j.envpol.2007.06.051

Lu, J., Getz, G., Miska, E. a, Alvarez-Saavedra, E., Lamb, J., Peck, D., Alejandro, S. C., Elbert, B. L., Mak, R. H., Ferrando, A. A., Downing, J. R., Jacks, T., Horvitz, H. R., Golub, T. R. (2005). MicroRNA expression profiles classify human cancers. *Nature, 435*, 834–8. doi: 10.1038/nature03702

MacKay, D., & Arnot, J. A. (2011). The application of fugacity and activity to simulating the environmental fate of organic contaminants. *Journal of Chemical and Engineering Data*, *56*, 1348–1355. doi: 10.1021/je101158y

Mackay, D., & Paterson, S. (1981). Calculating fugacity. *Environmental Science & Technology*, *15(*9), 1006–14. doi: 10.1021/es00091a001.

Maliszewska-Kordybach, B. (1999). Sources, concentrations, fate and effects of polycyclic aromatic hydrocarbons (PAHs) in the environment. Part A: PAHs in air. *Polish Journal of Environmental Studies*, *8*(3), 131–136.

Marce, R. M., & Borrull, F. (2000). Solid-phase extraction of polycyclic aromatic compounds. *Journal of Chromatography*, *885*, 273–290.

Marini, M., & Frapiccini, E. (2013). Persistence of polycyclic aromatic hydrocarbons in sediments in the deeper area of the Northern Adriatic Sea (Mediterranean Sea). *Chemosphere*, *90*, 1839–1846. doi: 10.1016/j.chemosphere.2012.09.080.

Maskaoui, K., & Hu, Z. (2009). Contamination and ecotoxicology risks of polycyclic aromatic hydrocarbons in Shantou coastal waters, China. *Bulletin of Environmental Contamination and Toxicology*, *82*(2), 172–178. doi: 10.1007/s00128-008-9522-6

McBride, M. B. (1994) Environmental Chemistry of Soils. New York: Oxford University Press.

Means, J. C. (1995). Influence of salinity upon sediment-water aromatic hydrocarbons. *Marine Chemistry*, *51*, 3–16.

Muckian, L., Grant, R., Doyle, E., & Clipson, N. (2007). Bacterial community structure in soils contaminated by polycyclic aromatic hydrocarbons. *Chemosphere*, *68*(8), 1535–1541. doi.org/10.1016/j.chemosphere.2007.03.029.

Nanuam, J., Sawangwong, P., & Pachana, K. (2011). The effects of varied pH on PAHs adsorption Thai clay minerals in synthetic sea water. *Journal of Science, Technology, and Humanities*, *9*(1), 1-7.

Nikolaou, A., Kostopoulou, M., Lofrano, G., & Meric, S. (2009). Determination of PAHs in marine sediment : analytical method and environment concern. *Global NEST Journal, 11*(4), 391–405.

OECD (1995). Organisation for Economic Co-operation and Development. Guideline for the testing of chemicals, partition coefficient (n-octanol/water): shake flask method. doi: 10.1787/9789264069626-en

Oh, S., Wang, Q., Shin, W. S., & Song, D. I. (2013). Effect of salting out on the desorption-resistance of polycyclic aromatic hydrocarbons (PAHs) in coastal sediment. *Chemical Engineering Journal*, *225*, 84–92. doi: 10.1016/j.cej.2013.03.069

Park, S. S., Kim, Y. J., & Kang, C. H. (2002). Atmospheric polycyclic aromatic hydrocarbons in Seoul , Korea. *Atmospheric Environment, 36*, 2917–2924.

Piatt, J. J., Backhus, D. A., Capel, P. D., & Eisenreich, S. J. (1996). Temperature-dependent sorption of naphthalene, phenanthrene, and pyrene to low organic carbon aquifer sediments. *Environmental Science and Technology*, *30*(3), 751–760. doi: 10.1021/es9406288

Plazinski, W., Dziuba, J., & Rudzinski, W. (2013). Modeling of sorption kinetics: The pseudo-second order equation and the sorbate intraparticle diffusivity. *Adsorption*, *19*, 1055–1064. doi: 10.1007/s10450-013-9529-0.

Qu, C., Li, B., Wu, H., Wang, S., & Giesy, J. P. (2015). Multi-pathway assessment of human health risk posed by polycyclic aromatic hydrocarbons. *Environmental Geochemistry and Health*, *37*, 587–601. doi: 10.1007/s10653-014-9675-7.

Samuillah, Y. (1990). Prediction of the environmental fate of chemical. England: Elsevier Science Publisher Ltd.

Shi, Z., Tao, S., Pan, B., Fan, W., He, X. C., Zuo, Q., Wu, S. P., Li, B.G., Cao, L., Liu, W. X., Xu, F. L., Wang, X. J., Shen, W. R., & Wong, P. K. (2005). Contamination of rivers in Tianjin, China by polycyclic aromatic hydrocarbons. *Environmental Pollution*, *134*, 97–111. doi: 10.1016/j.envpol.2004.07.014.

Shi, Z., Tao, S., Pan, B., Liu, W. X., & Shen, W. R. (2007). Partitioning and source diagnostics of polycyclic aromatic hydrocarbons in rivers in Tianjin, China. *Environmental Pollution*, *146*, 492–500. doi: 10.1016/j.envpol.2006.07.009.

Simpsona, C. D., Mosi, A. A., Reimerb, K. J., & Cullen, R. (1996). Composition and distribution of polycyclic aromatic hydrocarbon contamination in surficial marine sediments from Kitimat Harbor. *The Science of the Total Environment*, *181*, 265-278.

Sorlie, J. E., Huff, J., & Gillham, R. W. (1994). Evaluation of groundwater contamination potential of polycyclic aromatic hydrocarbons from ferromanganese sludge by leaching tests. *Groundwater Quality Management*, *220*, 183–192.

Srogi, K. (2007). Monitoring of environmental exposure to polycyclic aromatic hydrocarbons: a review. *Environmental Chemistry Letters*, *5*(4), 169–195. doi: 10.1007/s10311-007-0095-0

Sun, J.-H., Wang, G.-L., Chai, Y., Zhang, G., Li, J., & Feng, J. (2009). Distribution of polycyclic aromatic hydrocarbons (PAHs) in Henan Reach of the Yellow River, Middle China. *Ecotoxicology and Environmental Safety*, *72*, 1614–1624. doi: 10.1016/j.ecoenv.2008.05.010

Tahir, N. M., Fadzil, M. F., Ariffin, J., Maarop, H., & Wood, A. K. H. (2011). Sources of polycyclic aromatic hydrocarbons in mangrove sediment of Pulau Cik Wan Dagang, Kemaman. *Journal of Sustainability Science and Management*, *6*(1), 98–106. Universiti Malaysia Terengganu Publisher.

Tang, L., Tang, X.-Y., Zhu, Y.-G., Zheng, M.-H., & Miao, Q.-L. (2005). Contamination of polycyclic aromatic hydrocarbons (PAHs) in urban soils in Beijing, China. Environment International, *31*, 822–828. doi: 10.1016/j.envint.2005.05.031

Tang, N., Tabata, M., Mishukov, V. F., Sergineko, V., Toriba, A., Kizu, R., & Hayakawa, K. (2002). Comparison of atmospheric nitropolycyclic aromatic hydrocarbons in Vladivostok , Kanazawa and Toyama. *Journal of Health Science*, *48*(1), 30–36.

Tremblay, L., Kohl, S. D., Rice, J. a., & Gagné, J.-P. (2005). Effects of temperature, salinity, and dissolved humic substances on the sorption of polycyclic aromatic hydrocarbons to estuarine particles. *Marine Chemistry*, *96*, 21–34. doi: 10.1016/j.marchem.2004.10.004

Turner, A. (2003). Salting out of chemicals in estuaries: Implications for contaminant partitioning and modelling. *Science of the Total Environment*, 314-316, 599–612. doi: 10.1016/S0048-9697(03)00076-7

Ukiwe, L. N., Egereonu, U. U., Njoku, P. C., Nwoko, C. I. A., & Allinor, J. I. (2013). Polycyclic aromatic hydrocarbons degradation techniques: a review. *International Journal of Chemistry*, *5*(4), 43. doi: 10.5539/ijc.v5n4p43

Vela, N., Martínez-Menchón, M., Navarro, G., Pérez-Lucas, G., & Navarro, S. (2012). Removal of polycyclic aromatic hydrocarbons (PAHs) from groundwater by heterogeneous photocatalysis under natural sunlight. *Journal of Photochemistry and Photobiology* A: Chemistry, *232*, 32–40. doi: 10.1016/j.jphotochem.2012.02.003

Wang, C., Wang, F., Wang, T., Yang, X., Bian, Y., Kengara, F.O., Li, Zeng., Jiang, X. (2011). Effects of autoclaving and mercuric chloride sterilization on PAHs dissipation in a two-liquid-phase soil slurry. *Soil Science Society of China*, *21*, 56-64.

Wang, C., Wang, X., Gong, P., & Yao, T. (2014). Persistent organic pollutants in mountain air of the southeastern Tibetan Plateau: Seasonal variations and implications for regional cycling. *Environmental Pollution*, *194*, 210-21. doi: 10.1016/j.envpol.2014.08.002.

Wang, L., Niu, J., Yang, Z., Shen, Z., & Wang, J. (2008). Effects of carbonate and organic matter on sorption and desorption behavior of polycyclic aromatic hydrocarbons in the sediments from Yangtze River. *Journal of Hazardous Materials*, *154*, 811–817. doi: 10.1016/j.jhazmat.2007.10.096

Wang, L., Yang, Z., & Niu, J. (2011). Temperature-dependent sorption of polycyclic aromatic hydrocarbons on natural and treated sediments. *Chemosphere*, *82*, 895–900. doi:10.1016/j.chemosphere.2010.10.054

Whitehouse, B.G., 1984. The effects of temperature and salinity on the aqueous solubility of polynuclear aromatic-hydrocarbons. *Marine Chemicals*, *14*, 319–332

WHO (World Health Organization). (2000). Regional Office for Europe Copanhagen. Air Quality Guidelines for Europe Second Edition. WHO Regional Publications, European Series, No. 91.

Wild, S. R., & Jones, K. C. (1995). Aromatic hydrocarbons in the united kingdom environment : a preliminary source inventory and budget. *Environmental Pollution*, *88*, 91–108.

Wu, W., & Sun, H. (2010). Sorption–desorption hysteresis of phenanthrene – Effect of nanopores, solute concentration, and salinity. *Chemosphere*, *81*(7), 961–967. doi: 10.1016/j.chemosphere.2010.07.051

Xia, X. H., Yu, H., Yang, Z. F., & Huang, G. H. (2006). Biodegradation of polycyclic aromatic hydrocarbons in the natural waters of the Yellow River: Effects of high sediment content on biodegradation. *Chemosphere*, *65*, 457–466. doi: 10.1016/j.chemosphere.2006.01.075

Xu, J., Yu, Y., Wang, P., Guo, W., Dai, S., & Sun, H. (2007). Polycyclic aromatic hydrocarbons in the surface sediments from Yellow River, China. *Chemosphere*, *67*, 1408–1414. doi: 10.1016/j.chemosphere.2006.10.074

Zakaria, M. P., Takada, H., Tsutsumi, S., Ohno, K., Yamada, J., Kouno, E., & Kumata, H. (2002). Distribution of polycyclic aromatic hydrocarbons (PAHs) in rivers and estuaries in Malaysia: A widespread input of petrogenic PAHs. *Environmental Science and Technology*, *36*, 1907–1918. doi: 10.1021/es011278+

Zhang, J., Zeng, J., He, M. (2009). Effect of temperature and surfactants on naphthalene and phenanthrene sorption by soil. *Journal of Environmental Sciences* , *21*, 667-674.