# KINETICS AND MECHANISMS OF POLYAROMATIC HYDROCARBONS (PAH) SEQUESTRATION IN FRESHWATER AND MARINE SEDIMENT

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAH) are known to be persistant in marine and freshwater sediments. An aging process often called sequestration is responsible for the change in the availability of PAHs and is attributed to a slow migration of aromatic molecules into condensed organic matter and inaccessible microsites. To study the rate of PAH sequestration under laboratory conditions, natural sediment samples were spiked with [$^2$H]-PAH and labelled PAH were re-extracted periodically with an aqueous solution of a high molecular weight surfactant (Brij® 700) to estimate not sequestrated PAHs. Adsorbed molecules became slowly sequestered into inaccessible microsites and gradually more difficult to extract. A mathematical model was developed to quantify the rate constants of the sequestration process. The model was based on a three-compartment dynamic system in which aromatic compounds are taken up and sequestered by particulate matter. With the experimental conditions and the knowledge on diffusional process the three-compartment system was simplified to a first-order consecutive-irreversible two-stage reaction. The mean sequestration rate value of $k_2$ was ten times slower than the adsorption rate $k_1$.

RÉSUMÉ

Les hydrocarbures aromatiques polycycliques (HAPs) sont connus pour leur persistance dans les sédiments lacustres et marins. Un mécanisme de vieillissement souvent appelé séquestration est responsable du changement de biodisponibilité des HAPs et est attribué à une lente migration des molécules aromatiques dans la matière organique condensée et des microsites inaccessibles. Pour étudier la vitesse de séquestration des HAPs sous des conditions de laboratoire, nous avons ajouté des HAP marqués, [$^2$H]-HAPs, à des échantillons de sédiment naturel que nous avons ensuite périodiquement ré-extrait avec une solution aqueuse d'un tensio-actif de haut poids moléculaire (Brij® 700) afin d'estimer la proportion des HAPs non séquestrés. Les molécules adsorbées se sont lentement séquestrées dans des microsites inaccessibles et de plus en plus difficile à extraire. Un modèle mathématique a été développé pour quantifier les constantes de vitesse du mécanisme de séquestration. Le modèle est basé sur un système dynamique à trois compartiments dans lequel les composés aromatiques sont pris en charge et ensuite séquestrés par le matériel particulaire compte tenu des conditions expérimentales et de notre connaissance du processus diffusif, le système à 3 compartiments a été simplifié à une réaction de premier ordre à deux étapes consécutives et irréversibles. La vitesse moyenne de séquestration, $k_2$, est dix fois plus lente que la vitesse d'adsorption initiale, $k_1$.

## 1. INTRODUCTION

Although a large number of studies have been reported on the adsorption/desorption process of various PAHs on a large variety of lab-made particles and natural sediment or soil (Valsaraj et al.1999). The fate of hydrophobic organic compounds in natural water is dependent on their sorptive behaviour and PAHs are thus expected to remain sorbed to the sediment due to their non-ionic and hydrophobic properties (Schuler et al. 2001). Little is known about the kinetic of molecular diffusion phenomenon into sediment matrix and also on the first steps of sequestration process. The purpose of this study was to determine the kinetic of sequestration of PAHs such as phenanthrene-like structures (phenanthrene, pyrene, benzo(a)pyrene, benzo(ghi)perylene) and fluorene-like structures (fluorene, fluoranthene, benzo(k)fluoranthene) and also to investigate several factors such as the molecular structure or sediment characteristics that may influence sorption kinetics. These particular PAHs were chosen because of their major presence in the environment, and because they represent two different structural families. The phenanthrene-like structures are a composition of benzene ring and fluorene-like structures are composed of benzene ring with an incorporate five carbon ring. The PAH aromaticity determined by this difference between the ring composition might be determinant in sorption kinetics. Different factors can affect sequestration kinetics such as the amount of organic carbon or clay content present in soil or sediment. Pores are highly present in the organic fractions of soil and sorption of organic molecules such as PAHs in these pores is plausible (Alexander 2000). Sequestered compounds located in these pores are slowly desorbed and can reduce the availability. Organic carbon content in soil has also been found as a major determinant for aging (Nam et al., 1998). Authors have found that the bioavailability of phenanthrene to microorganisms was reduced after 200 days for soils with organic carbon content greater than 2%.

A kinetic model on the sequestration phenomenon based on a three-compartment model was adapted to evaluate the kinetic constants. Parameters as temperature, luminosity, microbial activity and the ratio PAH/sediment were controlled in order to reduce their influence in the kinetic process. This extraction technique determined the concentration of extractible labelled PAHs as a function of time and represented mainly the available PAH fraction

sorbed on sediment. Parameters such as grain size, carbon content, level of contamination, hydrophobicity were investigated as factors potentially affecting sequestration kinetics.


## 2. MATERIAL AND METHODS
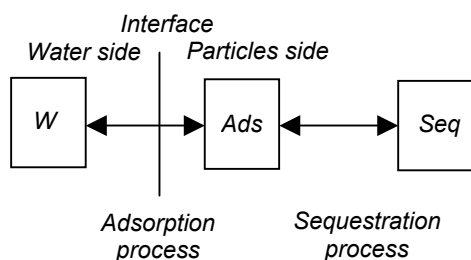
### 2.1 Kinetic model



Figure 1. Schematic diagram of thermodynamical three-compartmental model.


A three-compartmental thermodynamic system, as shown in Figure 1, can describe the adsorption and sequestration phenomenon of a solute on a particle in suspension in the solution. In this model, the first compartment $W$ is defined by the amount of dissolved PAHs which can be adsorbed to particles in the second compartment $Ads$ and finally sequestered in the compartment $Seq$. We hypothesized that surfactant solution extracted only extractible-adsorbed PAHs onto particles which represented the available fraction. In first approximation, it was assumed that adsorption was an irreversible reaction because of the high hydrophobicity of aromatic hydrocarbons. For a reduced availability of a molecule, the kinetic desorption must be slow. As a results, the slow rate of desorption from sequestered PAHs can be neglected on a short term period (time of the experiment) and then sequestration can be considered as an irreversible reaction. Working with these starting conditions the system was then defined as a first-order consecutive-irreversible two-stage reaction. A schematic diagram describing the transport of PAHs in this kinetic model is shown in Figure 2. $W$, $Ads$ and $Seq$ were the amount of PAHs in the respective compartment linked by two rate constant $k_1$ and $k_2$. This mechanism can be described by a set of three equations which can be solved for each compartment (mathematical equations not shown here).
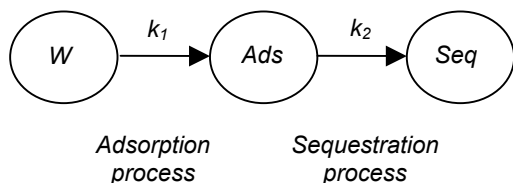


Figure 2. Schematic diagram of the three-compartmental kinetic model of sequestration.

Figure 3 describes the kinetic behaviour of the three compartments from the first-order consecutive-irreversible two-stage reaction model. Considering the kinetic of molecular diffusion resulting from the hydrophobicity driving force, the rate $k_1$ might be superior to $k_2$ because the intra particular molecular diffusion is a much more slower process. The rate constants were determined by a non-linear regression using the following equation and constraint:

$$y = \left(\frac{ab}{c-b}\right)(e^{-bx} - e^{-cx}) \; ; \; b > c \qquad [1]$$

The components $y$, $a$, $b$ and $c$ represent $[Ads]$, $[W]_0$, $k_1$ and $k_2$, respectively. $[W]_0$ represents the initial quantity of the reacting material and also the maximum amount of PAH to be sequestred with time.
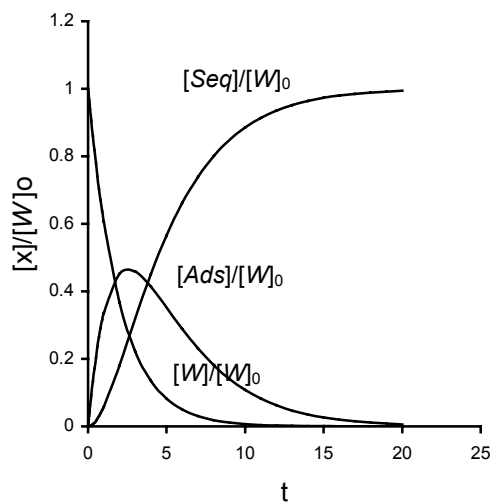


Figure 3. General aspect of the kinetic behaviour of the three compartments from the first-order consecutive-irreversible two-stage reaction model.


### 2.2 Sequestration experiments

Ten grams of wet sediment and 50 ml of deionised water were added into a 600 ml beaker. The slurry was sterilised with a germicidal lamp UV-C (254 nm) held at a distance of 15 cm from the water surface at 4°C for 48 hours. Sediment slurry was spiked with this 0.5 ml acetone solution of the 16 EPA [²H]-PAH cocktail and another 50 ml of deionised water was added giving a final PAH concentration of 100 µg/L. Beakers were then hermetically closed and slurries were stirred at 4°C in the dark for the time of the experiment. For short and long term kinetic experiments, [²H]-PAH were extracted periodically from the spiked sediment in the solution.

The sampling volume of sediment slurry spiked with labelled PAHs was 10 ml performed with a sterile pipet at intervals of 24h or 168h following the experiment. Spiked sediments were extracted with an aqueous solution of a high molecular weight surfactant (Brij®700) following a method described elsewhere (Barthe and Pelletier, 2003) and analysed by reverse-phase HPLC with fluorescence detection.

## 3. RESULTS AND DISCUSSION

Kinetic experiments were conducted on two very different sediment samples: one from a marine low contaminated site in the Baie des Ha!Ha! (Saguenay Fjord) (SAG09) and the other from a highly PAHs contaminated site (RIVC) in the Rivière Saint-Louis (Beauharnois, Que). The grain size distribution was roughly the same for both sediments but the content organic carbon was about 3.7 times higher in RIVC than in SAG09 sample.

Figure 4 presents the non linear regression results for benzo(a)pyrene (BaP) and fluorene for both sites. Each curve is the best fit of the concentration of extractable $[^2H]$-PAH as a function of elapsed time. As it can be seen, the amount of each $[^2H]$-PAH that can be extracted increases from zero to a maximum value between 0.12 an 0.24 µg/g following chemical compounds and sediments over a period 72 to 96 h. This first part of the curve describes the adsorption process of each $[^2H]$-PAH from compartment *W* to compartment *Ads*. As PAH molecules are only adsorbed at the surface of particles they are easy to extract with the surfactant solution and the extractable portion increases as the amount adsorbed increases for a given period of time. After this first adsorption step, the sequestration process becomes more efficient and slowly the amount of extractable $[^2H]$-PAHs starts to decrease following a pattern relatively similar for all PAHs tested. All curves tend toward an asymptotic value indicating that a small proportion of the sequestred $[^2H]$-PAHs will always be available at least under the present experimental conditions. Using the equation cited above, it became possible to calculate the kinetic parameters for each studied PAH and each sediment. These results are summarised in Table 1 and show how $[W]_0$, $k_1$, and $k_2$ changed with the structure and the size of the PAH molecule and the nature of the sediment tested. With freshwater contaminated sediment RIVC, smaller molecules such as phenanthrene, pyrene, fluorene and fluoranthene have higher $[W]_0$ and $k_1$ than bigger molecules such as benzo(ghi)perylene and benzo(k)fluorenthene. Rate constant $k_2$ defining the rate of sequestration is usually one order of magnitude smaller than $k_1$ standing for the rate of adsorption on to particles from the water compartment *W*.

The situation looks different for the low contaminated marine sediment (SAG09) where the nature of the PAH molecule seems not to be a determining factor in the sequestration process. $[W]_0$ is not decreasing in the increasing size of the molecules as seen with RIVC and even increased from fluorene to benzo(k)fluoranthene.



*BaP in RIVC*

$R^2 = 0.45$

*BaP in SAG09*

$R^2 = 0.76$

*Fluorene in RIVC*

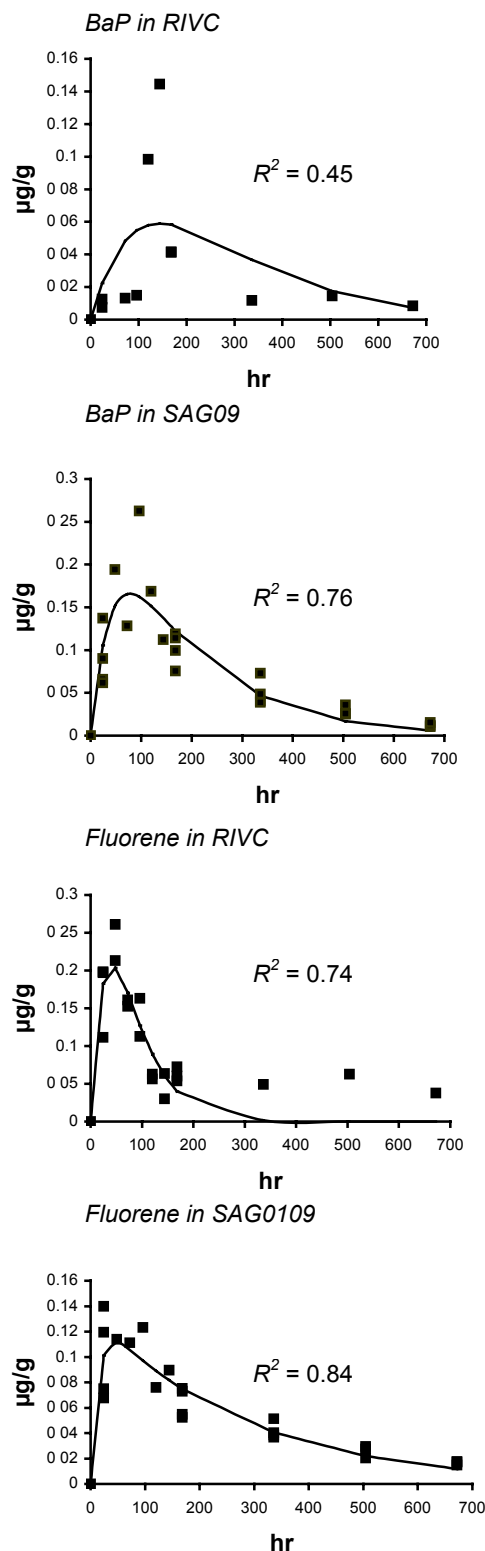$R^2 = 0.74$

*Fluorene in SAG0109*

$R^2 = 0.84$

Figure 4. Non linear regression (eq.1) results on experimental data on benzo(a)pyrene (BaP) and fluorene in RIVC and SAG0109 ($b = k_1$, $c = k_2$).

Table 1. Values (± SE) of kinetic parameters calculated from experimental data by non-linear regression analysis for the three compartment model.

| | RIVC | | | | SAG0109 | | | |
|---|---|---|---|---|---|---|---|---|
| | $[W]_0$ | $k_1$ | $k_2$ | $R^2$ | $[W]_0$ | $k_1$ | $k_2$ | $R^2$ |
| Phenanthrene | 0.277 ±0.070 | 0.056 ±0.039 | 0.006 ±0.003 | 0.45 | 0.267 ±0.031 | 0.037 ±0.011 | 0.003 ±0.001 | 0.76 |
| Pyrene | 0.187 ±0.030 | 0.040 ±0.019 | 0.002 ±0.001 | 0.48 | 0.217 ±0.023 | 0.045 ±0.013 | 0.0025 ±0.0005 | 0.72 |
| B(a)p | 0.132 ±0.057 | 0.017 ±0.013 | 0.003 ±0.003 | 0.45 | 0.266 ±0.062 | 0.023 ±0.009 | 0.006 ±0.002 | 0.76 |
| Bz(ghi)peryle. | 0.122 ±0.034 | 0.023 ±0.015 | 0.002 ±0.002 | 0.42 | 0.173 ±0.024 | 0.033 ±0.011 | 0.0024 ±0.0006 | 0.62 |
| Fluorene | 0.474 ±0.565 | 0.029 ±0.040 | 0.020 ±0.026 | 0.77 | 0.131 ±0.013 | 0.070 ±0.023 | 0.0037 ±0.0007 | 0.84 |
| Fluoranthene | 0.193 ±0.047 | 0.029 ±0.015 | 0.004 ±0.002 | 0.54 | 0.221 ±0.022 | 0.039 ±0.010 | 0.0026 ±0.0005 | 0.77 |
| B(k)fluoranthe. | 0.011 ±0.027 | 0.024 ±0.014 | 0.001 ±0.001 | 0.44 | 0.226 ±0.029 | 0.039 ±0.010 | 0.0027 ±0.0007 | 0.69 |

Units of rate constant : $h^{-1}$

Both $k_1$ and $k_2$ do not show any peculiar trend as a function of the shape and the size of the PAH molecules. Again the sequestration rate, $k_2$, is still roughly one order of magnitude lower than the adsorption rate. It should also be observed that correlation coefficient ($R^2$) of best-fitting curves are usually better in sediment SAG09 than RIVC. That might be partly attributed to a reduced number of data available for RIVC, but it seems also reflect the presence of a more complex sedimentary environment where the presence of a high level of organic matter and indigenous PAHs seem to play a determining role on the kinetic parameters.

These results are currently under investigation and efforts are deployed to determine which physical and chemical factors are responsible for the difference observed between molecules and between sediments. There is an attempt to understand sequestration mechanisms using available models already available in the scientific literature (Luthy et al. 1997).

4. CONCLUSION

A three-compartment kinetic model based on the hypothesis that a surfactant extraction can be representative of the availability of PAHs adsorbed to the surface of sediment particles allowed the determination of sequestration rate constants for seven PAHs in two natural sediments. The results suggest that dissolved [$^2$H]-PAHs are first adsorbed onto the surface of particles within a 4-7 day period as a function of their molecular weight and hydrophobicity, and also sediment characteristics. Secondly, adsorbed molecules became slowly sequestered and the sequestration process seems to be almost completed over a period of 2-3 weeks. It is also possible with this model and the value of [$W$]$_0$ to calculate the time needed to reach a 5 % extractible PAHs. In summary, our results reveal for

the first time that the rate at which a know process of sequestration is proceeding with untreated natural sediments and under conditions (low temperature, absence of light, no bacterial activities) close to those encountered in northern environments and deep Saguenay Fjord.

5. REFERENCES

Alexander, M. 2000. Aging, bioavailability, and overestimation of risk from environmental pollutants. *Environ. Sci. Technol.* 34:4259-4265.

Barthe, M. and Pelletier, É. 2003. Selective extraction of polycyclic aromatic hydrocarbons (PAHs) from contaminated sediments using a high molecular weight surfactant. Proceeding 2nd International Symposium on *Contaminated Sediments: Characterization, Evaluation, Mitigation/ Restoration, and Management Strategy Performance,* Québec, Canada.

Nam K., Chung N., Alexander M., 1998. Relationship between organic matter content of soil and the sequestration of phenanthrene. *Environ. Sci. Technol.* 32:3785-3788.

Luthy R.G., Aiken G.R., Brusseau M.L., Cunnigham S.D., Gschwend P.M., Pignatello J.J., Reinhard M., Traina S.J., Weber W.J., Westall J.C. 1997. Sequestration of hydrophobic contaminants by geosorbents. *Environ. Sci. Technol.* 31:3341-3347.

Schuler L.J., Lydy M.J. 2001. Chemical and biological availability of sediment-sorbed benzo(a)pyrene and hexachlorobiphenyl. *Environ. Toxicol. Chem.* 20:2014-2020.

Valsaraj K.T., Thibodeaux L.J. 1999. On the linear driving force model for sorption kinetics of organic compounds on suspended sediment particles. *Environ. Toxicol. Chem.* 18:1679-1685.