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Sediment-Water Exchange, Spatial Variations, and Ecological Risk Assessment of Polycyclic Aromatic Hydrocarbons (PAHs) in the Songhua River, China

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Abstract: The sediment-water exchange, spatial variations, and ecological risk of polycyclic aromatic hydrocarbons (PAHs) in the water and sediment of the Songhua River, China, were investigated and assessed in this paper. The fugacity fraction (*ff*) was used to evaluate the sediment–water exchange of PAHs between the water and sediment. The results suggest that the values of *ff* decreased with an increasing number of PAH rings. The sediment acts as a secondary emission source for three- and four-ring PAHs, whereas five-ring PAHs were deposited in the sediment from the water. The high *ff* values of PAHs found in autumn suggest large releases of PAHs after abundant deposition in summer, and the lowest *ff* values of PAHs occurred in summer. The values were especially low for five- and six-ring PAHs, which exhibited considerable deposition from the water to the sediment. PAHs with low molecular weights showed strong variations, which were potentially caused by their active physical-chemical properties. Additionally, high molecular weight BaP displayed weak variations, increasing the potential risk in the sediment. The simplified qualitative method of $C_{water}/C_{sediment}$ is useful for assessing variations in the sediment–water exchange. The relationships between $C_{water}/C_{sediment}$ and *ff* were investigated by determining the Pearson correlation coefficients (R). The results exhibited a significant negative correlation, with $R = -1.000$ and $P = 0.000$ for Flu, $R = -0.993$ and $P = 0.007$ for Phe, $R = -0.998$ and $P = 0.002$ for FlA, and $R = -0.971$ and $P = 0.029$ for BaP. The coefficients of variation indicated that five-ring PAHs were more sensitive than three- and four-ring PAHs. Thus, these low-ring PAHs can be easily exchanged between the sediment and the water. Additionally, the ecological risk of PAHs to aquatic organisms in the Songhua River is relatively low.

Keywords: PAHs; fugacity approach; spatial variations; ecological risk; Songhua River

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous hydrophobic organic pollutants that can enter the environment through natural processes and anthropogenic activities [1]. PAHs have been recognized as major environmental and health threats because of their potential bioaccumulation, mutagenic, and carcinogenic effects on organisms and humans [2,3]. Coal combustion and automobile emissions are the major anthropogenic sources of PAHs, especially in economically developed areas, areas of large energy consumption, and cold regions [4]. In aquatic environments, PAHs are mainly derived from atmospheric deposition, municipal and industrial effluents, land run-off, and oil spills or leakage [5–7]. Recently, the quality of the aquatic environment has attracted considerable attention due to the associated ecological risks, which are influenced by rapid urbanization and industrialization in China [8].

Located in northeastern China, the Songhua River is one of the major rivers in the country. It plays important roles in economics, transportation, tourism, and irrigation because it supplies drinking water and irrigation water for one of the most important food production bases in China [9,10]. Recently, various organic pollutants, such as PAHs, polychlorinated biphenyls (PCBs), and organochlorine pesticides (OCPs), have been introduced into the water and sediment of the Songhua River [11–13]. The Songhua River has become one of the most severely polluted rivers in China because petrochemical industries are located in the Songhua River Basin, coal combustion is more common in this cold temperature zone than along rivers in southern China, and pesticides are regularly applied to agricultural products [14,15].

Recent studies have focused on the soil–air, air–water, and sediment–water exchanges of typical persistent organic pollutants (POPs), such as PCBs, OCPs, and PAHs [16–25]. Generally, sediments act as a source or sink of POPs; thus, the sediment–water exchange may affect the quality of surface waters because contaminants can be released from the sediment when they are not in equilibrium with the water [25]. Therefore, managing the PAH levels in contaminated water bodies requires an adequate understanding of the migration and exchange processes between the sediment and the water [26].

To date, no comprehensive research on PAH pollution has been performed in the Songhua River, especially regarding the exchange, migration, and transfer of PAHs between the sediment and the water. However, an understanding of the mechanisms of the sediment–water exchange of PAHs could be used to guide the evaluation, development, and improvement of policies and measures that control and reduce PAH levels in the environment. In particular, the seasonal exchange mechanisms of PAHs between sediments and water are not well understood. Hence, the objectives of this study are as follows: (1) to investigate the sediment-water exchange of PAHs in the Songhua River; (2) to explore the spatial variation characteristics of PAHs; and (3) to assess the potential ecological risks of PAHs in the water and sediments of the Songhua River.

2. Methodology

2.1. Study Area

The Songhua River extends from 41°42′ N to 51°48′ N and from 119°52′ E to 132°31′ E. It is one of the seven largest rivers in China, with a catchment area of ~556,800 km^2 [10,11]. With a length of 1970 km, the Songhua River is one of the largest tributaries of the Heilongjiang River, which comprises the Second Songhua River, the Nen River, and the main channel of the Songhua River (Figure 1). This area has a temperate continental monsoon climate, and the average temperature is −19 °C in January and 23 °C in July. Recently, the environmental qualities of the water and sediments in the Songhua River have been critically affected by pollutants due to rapid urbanization, industrial and agricultural development, and frequent environmental pollution events. Thus, it is necessary to investigate and explore the environmental behaviors of PAHs, which are abundant pollutants due to their broad range of sources and wide distribution, in order to control and improve the quality of the aquatic environment. Sampling sites were selected to represent the different industrial processes and human activities in the study area. A detailed map of the sampling sites is presented in Figure 1.

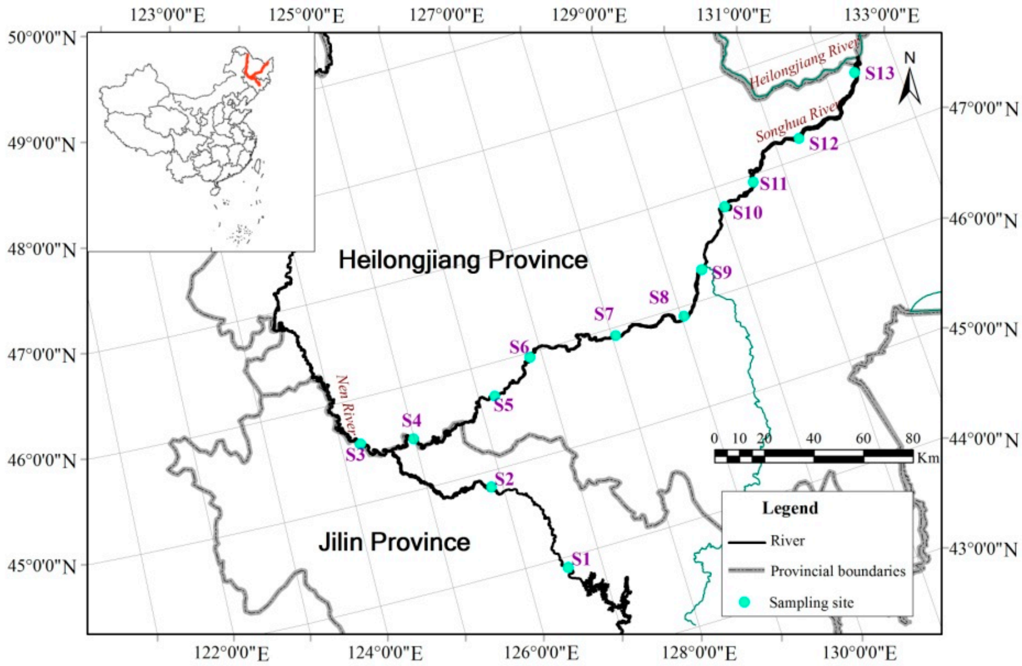


Figure 1. Map of the sampling sites.

2.2. Data Sources and Compilation

In this study, PAH concentration data were collected and compiled from the sediments and water by our research group (International Joint Research Center for Persistent Toxic Substances) during different monitoring periods. The average seasonal concentrations of 15 PAHs (Acy, acenapthylene; Ace, acenapthene; Flu, fluorene; Phe, phenanthrene; Ant, anthracene; FlA, fluoranthene; Pyr, pyrene; BaA, benz[a]anthracene; Chr, chrysene; BbF, benzo[b]fluoranthene; BkF, benzo[k]fluoranthene; BaP, benzo[a]pyrene; IcdP, indeno[l,2,3-cd]pyrene; DahA, dibenz[a,h]anthracene; and BghiP, benzo[g;h;i]perylene) are presented in Figure 2. Samples were collected in spring (April), early summer (May), summer (July) and autumn (October), but no sediment samples were collected in winter. Details regarding the analytical procedures used for sediment and water sampling are provided in the references [11,25], and site locations are shown in Figure 1. The mean value of the total organic carbon (TOC) content in the sediment is 0.89%, with values ranging from 0.32% to 1.68%. Detailed information regarding TOCs is presented in the references [11,25].

Note that the seasonal PAH concentrations in the sediment and water of the Songhua River vary according to the sampling time. However, the samples were concurrently collected from the sediment and water; therefore, we expect the data sets to demonstrate similar seasonal variations.

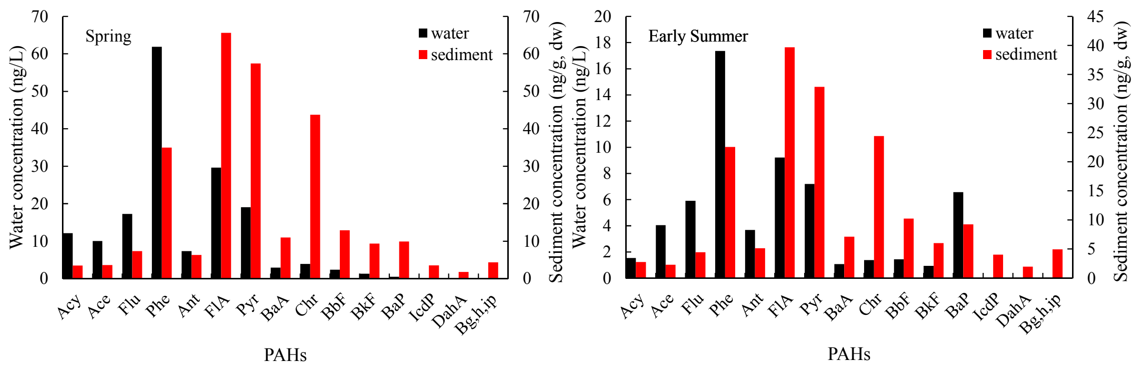


Figure 2. *Cont.*

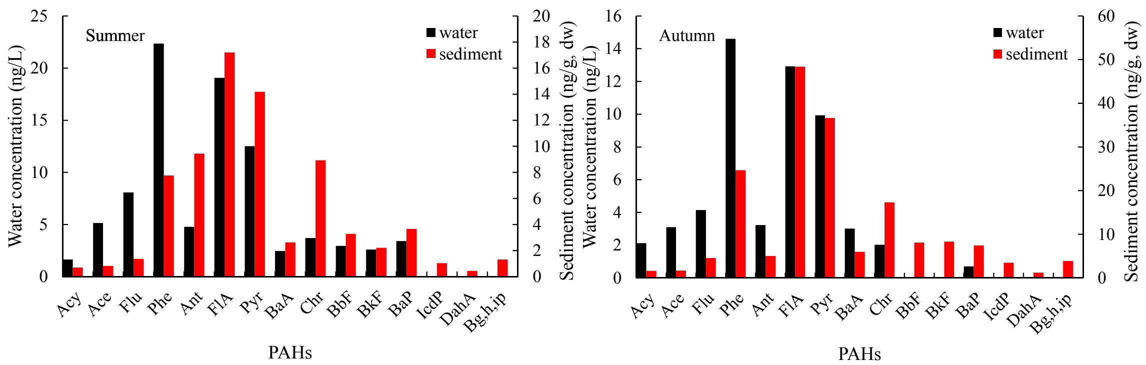


Figure 2. Average PAH concentrations exhibiting seasonal variations in the sediment and water of the Songhua River.

2.3. Fugacity Fraction Calculation

A fugacity approach was used to evaluate the equilibrium states of the organic pollutants and to better understand the sediment–water exchange processes of PAHs. Generally, the movement of chemicals from one medium to another is represented by fugacity, which controls the transfer of chemicals between media [27]. The fugacity is related to the concentrations of organic pollutants and the fugacity capacity of the corresponding environmental medium:

$$f = C_{\mathrm{mol}}/Z \tag{1}$$

where f is the fugacity of the organic pollutant in Pa, Z is the fugacity capacity of the specific medium in mol·m^{-3}·Pa^{-1}, and C_{mol} is the molar concentration of the organic pollutant in mol·m^{-3}. However, the concentrations of organic pollutants in the sediments and water were monitored in ng·g^{-1} and ng·L^{-1}, respectively. Hence, the quality concentrations were converted to the corresponding molar concentrations as follows:

$$C_{\mathrm{sedi,mol}} = 10^6 C_s \rho_{s1}/P_{\mathrm{mol}} \tag{2}$$

$$C_{\mathrm{water,mol}} = 10^6 C_w/P_{\mathrm{mol}} \tag{3}$$

where $C_{\mathrm{sedi,mol}}$ and $C_{\mathrm{water,mol}}$ are the molar concentrations of organic pollutants in the sediment and water, respectively. C_s is the measured mass concentration in the sediment in ng·g^{-1} dw (dry weight), C_w is the measured mass concentration in the water in ng·L^{-1}, ρ_{s1} is the density of the sediments in kg·m^{-3}, and P_{mol} is the molar mass of an organic pollutant in g·mol^{-1}.

The fugacity capacities of the sediment (Z_{sedi}) and water (Z_{water}) can be expressed as follows:

$$Z_{\mathrm{sedi}} = K_p \times \rho_{s2}/H = 0.41 \times f_{oc} K_{ow}\, \rho_{s2}/H \tag{4}$$

$$Z_{\mathrm{water}} = 1/H \tag{5}$$

$$K_p = 0.41 \times f_{oc} K_{ow} \tag{6}$$

where H is the Henry's law constant in Pa·m^3·mol^{-1}, K_{ow} is the dimensionless partition coefficient of octanol-water, f_{oc} is the organic carbon fraction in the sediment, ρ_{s2} is the density of the sediment in kg·L^{-1}, and K_p is the partition coefficient in L·kg^{-1}.

The fugacities of the sediment (f_{sedi}) and water (f_{water}) can be expressed as follows:

$$f_{\mathrm{sedi}} = C_{\mathrm{sedi,mol}}/Z_{\mathrm{sedi}} = \frac{10^6 C_s \rho_{s1}/P_{\mathrm{mol}}}{0.41 \times f_{oc} K_{ow} \rho_{s2}/H} \tag{7}$$

$$f_{\text{water}} = C_{\text{water,mol}}/Z_{\text{water}} = \frac{10^6 C_W/P_{\text{mol}}}{1/H} \tag{8}$$

The numerical relationship between ρ_{s1} and ρ_{s2} can be simplified as $\rho_{s1} = 1000\rho_{s2}$.

The fugacity fraction (*ff*) is used to assess the equilibrium states and exchange behaviors of chemicals or PAHs between the sediment and water.

$$ff = \frac{f_{\text{sedi}}}{f_{\text{sedi}} + f_{\text{water}}} = \frac{C_s\rho_{s1}/0.41 \times f_{oc}K_{oW}\rho_{s2}}{C_s\rho_{s1}/0.41 \times f_{oc}K_{oW}\rho_{s2} + C_W} = \frac{1000C_s/0.41 \times f_{oc}K_{oW}}{1000C_s/0.41 \times f_{oc}K_{oW} + C_W} \tag{9}$$

Sediment-water equilibrium suggests that the values of *ff* are equal to 0.5; thus, the net diffusion flux is zero. Values of *ff* > 0.5 indicate migration from the sediment to the water. In this case, the sediment acts as a secondary emission source. Values of *ff* < 0.5 indicate the deposition of PAHs from the water to the sediment. In this case, the sediment acts as a sink.

3. Results and Discussion

3.1. Sediment–Water Exchange

3.1.1. General Variations

The PAH concentrations in the sediment and water associated with K_{ow} values were used to evaluate the equilibrium states of individual PAHs (Table 1). The concentrations of PAHs, including the minimum, maximum, and mean values, were calculated using the entire data set. Values of log K_{ow} were derived from Mackay [28] and the US EPA EPI Suite™ [29]. The EPI Suite™ is facilitated by a database of more than 40,000 chemicals derived from the PHYSPROP© database [30]. K_{ow} is generally related to temperature, which is a key parameter of chemical partitioning between the aquatic and organic phases. Jensen et al. suggested that the bioconcentration factor (BCF) was in accordance with K_{ow}, potentially threatening aquatic organisms [31].

Table 1. Concentrations of PAHs in the sediment (ng·g^{-1}, dw) and water (ng·L^{-1}), the logarithm of the octanol-water partition coefficient (LogK_{ow}), and fugacity fractions (*ff*) of different organic carbon contents.

PAHs	LogK_{ow}	Water				Sediment				*ff*			*ff* 0.32% OC	*ff* 1.68% OC
		min	max	mean	Std.	min	max	mean	Std.	min	max	mean	mean	mean
Acy	3.94	1.53	12.18	4.37	5.21	0.70	3.48	2.15	1.23	0.83	0.98	0.95	0.98	0.89
Ace	3.92	3.10	10.07	5.58	3.10	0.83	3.64	2.11	1.18	0.86	0.96	0.94	0.97	0.87
Flu	4.18	4.15	17.32	8.86	5.86	1.37	7.36	4.43	2.45	0.80	0.94	0.91	0.96	0.83
Phe	4.46	14.60	61.86	29.04	22.11	7.77	35.00	22.49	11.22	0.74	0.93	0.89	0.95	0.80
Ant	4.54	3.23	7.37	4.76	1.86	5.02	9.45	6.48	2.07	0.84	0.97	0.93	0.97	0.85
FlA	5.22	9.22	29.62	17.70	8.92	17.21	65.60	42.70	20.13	0.66	0.90	0.82	0.92	0.68
Pyr	5.18	7.19	19.08	12.18	5.09	14.18	57.45	35.28	17.74	0.74	0.91	0.86	0.94	0.74
BaA	5.61	1.08	3.01	2.37	0.90	2.62	10.99	6.68	3.45	0.57	0.82	0.69	0.84	0.50
Chr	5.91	1.37	3.97	2.76	1.27	8.93	43.74	23.60	14.84	0.66	0.86	0.77	0.89	0.60
BbF	6.57	0.00	2.94	1.69	1.29	3.28	12.90	8.63	4.07	0.15	1.00	0.30	0.51	0.17
BkF	6.84	0.00	2.60	1.21	1.08	2.20	9.42	6.49	3.19	0.07	1.00	0.20	0.37	0.10
BaP	6.4	0.54	6.57	2.81	2.84	3.66	9.97	7.58	2.82	0.08	0.67	0.25	0.45	0.14
IcdP	7.66	0.00	0.00	0.00	0.00	1.03	4.03	3.02	1.35	1.00	1.00	1.00	1.00	1.00
DahA	6.5	0.00	0.00	0.00	0.00	0.43	1.96	1.35	0.69	1.00	1.00	1.00	1.00	1.00
Bg,h,ip	7.1	0.00	0.02	0.01	0.01	1.32	4.94	3.64	1.60	0.71	1.00	0.94	0.97	0.88

Table 1 shows the fugacity fractions (*ff*) of individual PAHs between the sediment and water in the Songhua River, China. The general variation indicates that the values of *ff* decreased with increasing PAH rings, except for IcdP and DahA, which were not detected in the water. The mean values of *ff* for PAHs with low molecular weights, including three- and four-ring PAHs, were greater than or equal to 0.7. These values suggest that the sediment acts as a secondary emission source for these PAHs. However, the minimum values of *ff* for FlA, BaA, and Chr were 0.66, 0.57, and 0.66, respectively, suggesting that these PAHs are situated between equilibrium and non-equilibrium states. The values of *ff* for BbF, BkF, and BaP were less than or equal to 0.3, indicating that five-ring PAHs were deposited in the sediment from the water. Thus, the sediment acted as a sink that accumulated

PAHs, reducing the amount of high-toxicity pollutants, especially BaP, in the water. Generally, the propagated errors in the calculated fugacity fractions of the sediment–water exchange of PAHs suggest that fugacity fractions between 0.3 and 0.7 represent an equilibrium state in the adjacent environmental medium [32–34]. In addition, the mean value of BghiP was 0.94, which was similar to the values of PAHs with low molecular weights, suggesting that these PAHs may be affected by the BghiP concentration in water. Therefore, the concentrations of PAHs in the sediment and water can affect the behavior of the sediment–water exchange.

3.1.2. Seasonal Variations in PAHs

Seasonal variations in PAH concentrations in the sediment and water of the Songhua River were evaluated and compiled, as presented in Figure 2. The seasonal *ff* values of PAHs were calculated according to the concentrations and average organic carbon contents, which are illustrated in Figure 3. The high *ff* values of PAHs in autumn suggest large releases after the deposition of large amounts of PAHs in summer. The lowest *ff* values of PAHs occurred in summer. Five- and six-ring PAHs, including BbF, BaP, IcdP, DahA, and BghiP, were particularly abundant, representing considerable deposition from the water to the sediment. In addition, IcdP, DahA, and BghiP had higher *ff* values in spring, early summer, and autumn because their concentrations in water were not detectable or low, directly affecting the equilibrium status between the sediment and the water.

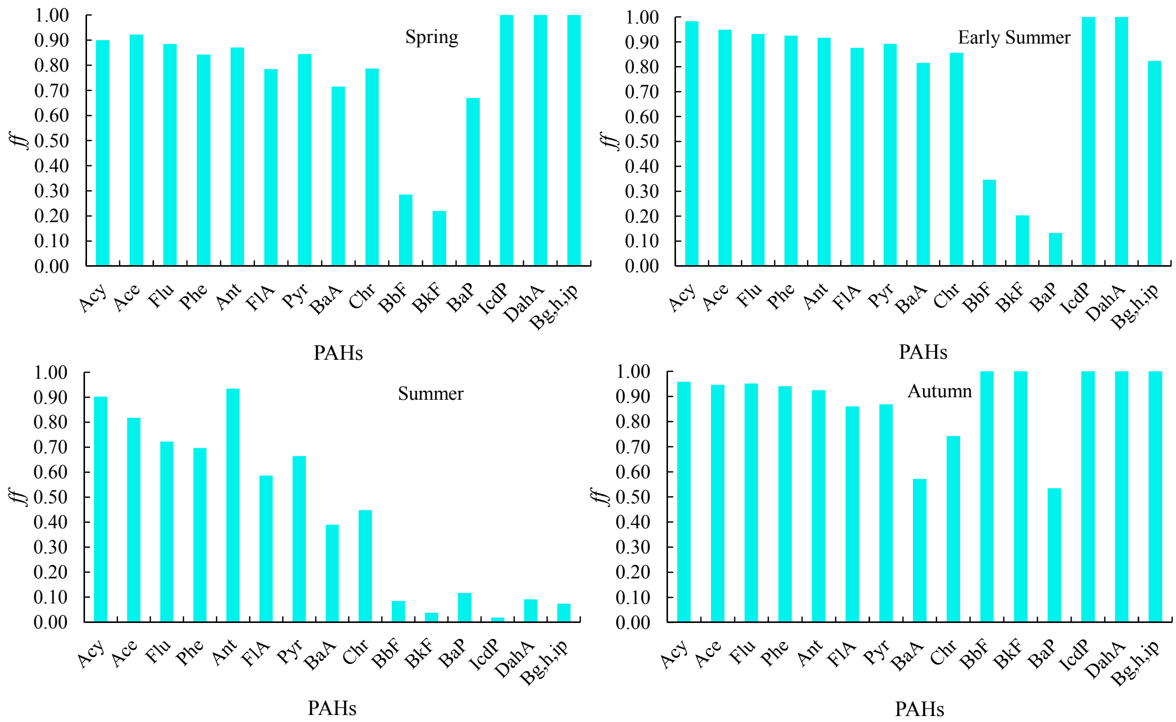


Figure 3. Seasonal variations in the fugacity fractions of PAHs.

Generally, the environmental behaviors of organic pollutants are associated with temperature, and high temperatures can rapidly release pollutants from relatively stable media. Lang et al. suggested that temperature and precipitation are the most important parameters controlling the seasonality in the PAH concentrations [35]. The various environmental characteristics of PAHs were observed in this study, and the *ff* of the sediment–water exchange demonstrated dynamic variations. Figure 4 depicts the seasonal variations in *ff* for three- and five-ring PAHs, including Flu, Phe, FlA, and BaP. Flu, Phe and FlA exhibited inverted "S"-type curves, while BaP displayed a "U"-type curve. These curves show the regularity of the variation in the sediment-water exchange. The PAHs with low molecular weights exhibited the largest variations, possibly due to their active physical-chemical properties. However, the high molecular weight BaP displayed weak variation, potentially increasing the risk in the sediment because it is relatively stable in sediment compared with water.

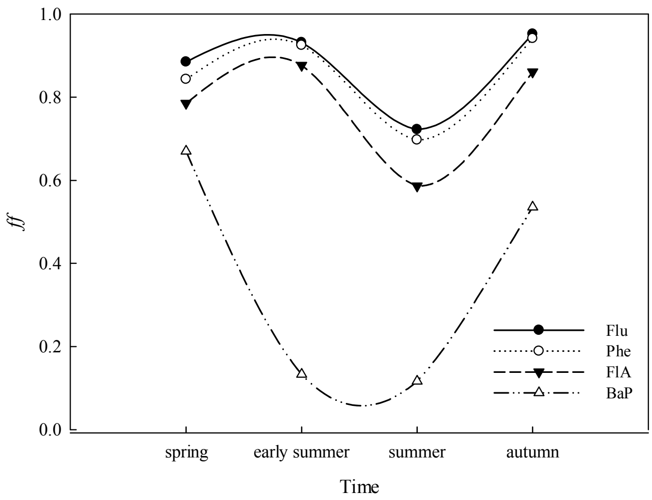
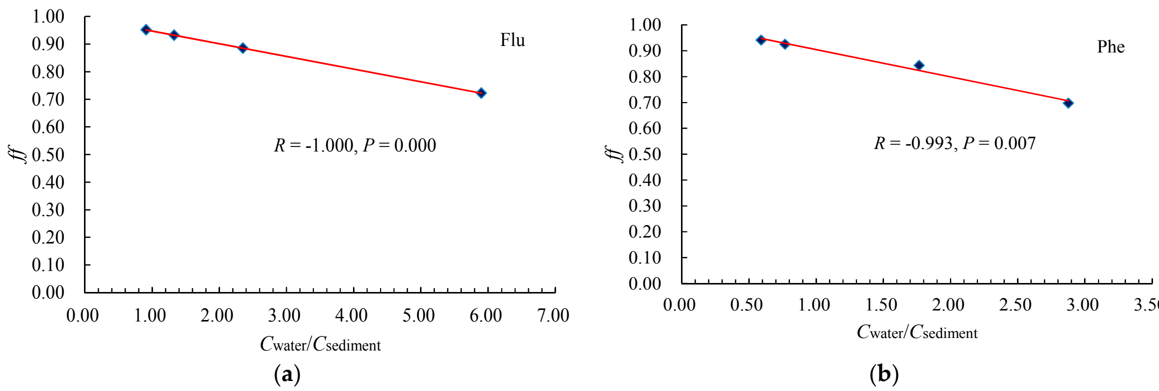


Figure 4. Seasonal variations in the *ff* values of Flu, Phe, FlA, and BaP.

3.1.3. Influence of Concentration on the Sediment–Water Exchange

Generally, sources of PAHs are widespread in the environment, and these sources affect concentrations and exchange behaviors in different environmental media. Differences in PAH concentrations in adjacent environmental media can also influence net flux trends [36], i.e., differences in PAH concentrations between the sediment and water can affect PAH migration, transfer, and diffusion variations.

The concentration ratios of PAHs between the water and sediment ($C_{water}/C_{sediment}$) were introduced to understand the effects of PAH concentrations on the associated exchange behaviors. The relationships between $C_{water}/C_{sediment}$ and *ff* were investigated by determining the Pearson correlation coefficients (*R*). The results exhibited a significant negative correlation, with $R = -1.000$ and $P = 0.000$ for Flu, $R = -0.993$ and $P = 0.007$ for Phe, $R = -0.998$ and $P = 0.002$ for FlA, and $R = -0.971$ and $P = 0.029$ for BaP (Figure 5). The simplified qualitative method of $C_{water}/C_{sediment}$ is useful for assessing variations in the sediment–water exchange; however, it is only suitable for comparing the degree of sediment–water exchange over a period, such as seasonal variations or time series data. It cannot be applied to determine the equilibrium states of PAHs because they are generally associated with concentrations, the organic carbon content in the sediment, the physical-chemical properties of PAHs, etc.



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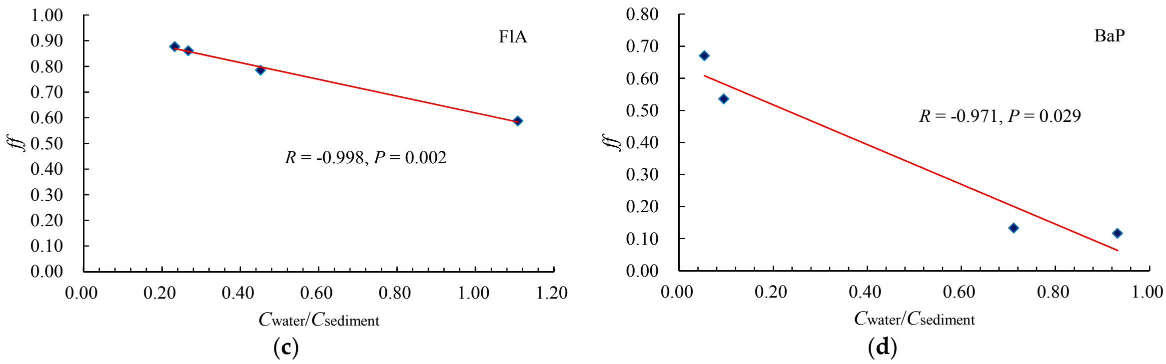

Figure 5. Relationship between the concentration ratio of water and sediment ($C_{water}/C_{sediment}$) and the fugacity fraction. (**a**) Flu; (**b**) Phe; (**c**) FlA and (**d**) BaP.

3.1.4. *ff* Response to Variations in Organic Carbon

The physical-chemical properties of PAHs generally affect their exchange between sediments and water at certain organic carbon contents and PAH concentrations. Thus, the response coefficient (*RC*) was introduced to explore the influence of organic carbon exchange on *ff* values of individual PAHs and evaluate the sediment–water exchange of PAHs:

$$RC = (ff_{\mathrm{min}oc} - ff_{\mathrm{max}oc})/ff_{\mathrm{mean}oc} \quad (10)$$

where $ff_{\mathrm{min}oc}$, $ff_{\mathrm{max}oc}$, and $ff_{\mathrm{mean}oc}$ are the *ff* values of PAHs corresponding to the minimum (0.32%), maximum (1.68%), and mean values (0.89%) of organic carbon contents, respectively. The *ff* values of individual PAHs are presented in Table 1. Generally, *RC* is proportional to the *ff* values of PAHs. Figure 6 depicts the *RC* values of individual PAHs, excluding IcdP, DahA, and BghiP, at varying organic carbon contents.

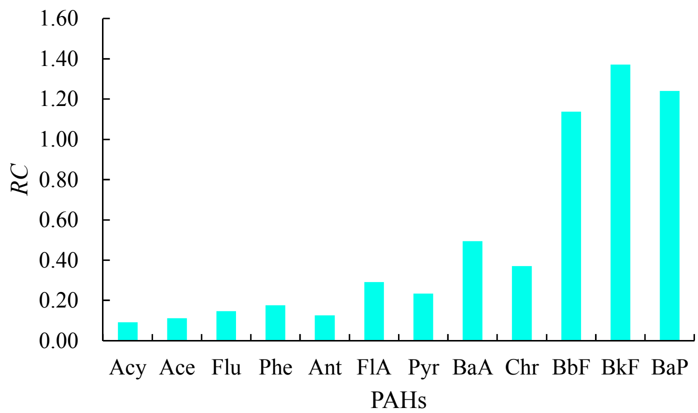

Figure 6. Response coefficients of individual PAH fugacity fractions to organic carbon contents.

Figure 6 shows that the five-ring PAHs, including BbF, BkF, and BaP, were more sensitive than the three- and four-ring PAHs because they have high solubility and low K_{ow} values, allowing easy sediment–water exchange. Thus, the organic carbon content can considerably affect the sediment–water exchange of PAHs with high molecular weights.

3.2. Spatial Variations of PAHs

Spatial heterogeneity is an essential characteristic of organic pollutants and is influenced by numerous factors. The contamination characteristics of PAHs in water and sediment can reflect processes such as industrial and economic development, the levels of control and regulation of organic pollutants, and signs of human activity [13]. For example, high pollution levels have been reported in water and sediment due to an abundance of pollution sources, a large population, a large energy consumption structure, and the presence of an industrial district [37–40]. In addition, the water flow, current velocity, total organic carbon level, and topographical conditions may also influence the adsorption, horizontal distribution, transport, and migration of pollutants, thereby affecting the levels of pollutants in the water and sediment [41–43].

The spatial heterogeneity of the sources and distribution of PAHs in the Songhua River, located in a cold region of China where heating is required in the winter, was investigated. The coefficient of variation (C_V) was employed to study the spatial heterogeneity, and the C_V values of PAHs in the water and sediment of the Songhua River at the 13 sampling sites reflect the characteristics of the PAH sources to some extent.

The coefficient of variation is defined as the ratio of the standard deviation σ to the mean μ [44].

$$C_V = \frac{\sigma}{\mu} \quad (11)$$

The coefficient of variation can be used to compare the degree of variation between data series, even if the means are drastically different. Generally, $C_V \leqslant 0.1$ corresponds to weak variability, $0.1 < C_V < 1$ corresponds to moderate variability, and $C_V \geqslant 1$ corresponds to strong variability.

We focused on the spatial distribution of water and sediment data from early summer because there are almost no missing PAH data from the 13 sampling sites during the early summer sampling period. Figure 7 illustrates the heterogeneous spatial distribution of PAH sources in the water and sediment of the Songhua River. Large variations in C_V occur in water compared to those in the sediment, especially for PAHs with high molecular weights, which have larger degrees of dispersion in both the water and sediment and may originate from point source emissions or discharge at certain sampling sites. In contrast, three- and four-ring PAHs displayed moderate dispersion in the water, potentially indicating similar PAH sources. Hence, the spatial heterogeneity of PAHs in the Songhua River is mainly associated with the malconformation of the energy consumption structure, the level of economic development, and human activities, which can directly lead to spatial differences in PAHs.

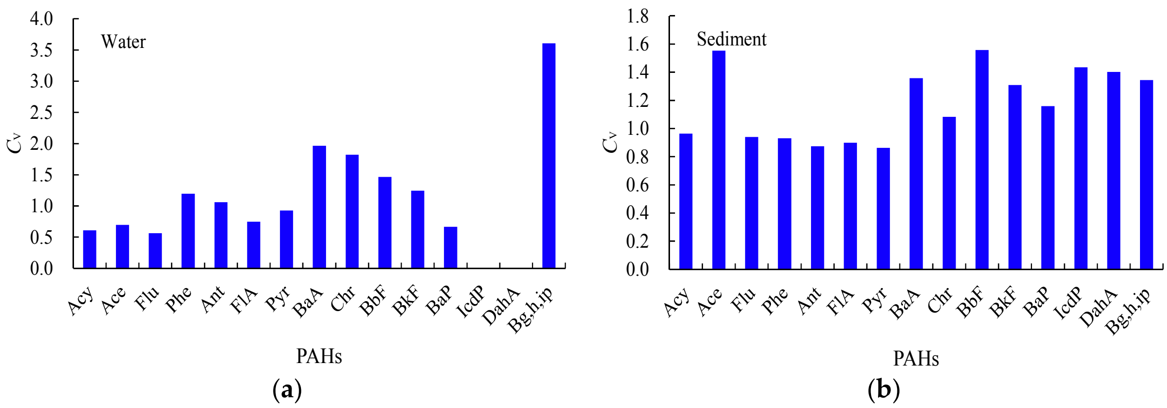

Figure 7. Coefficient of variation of PAHs in the water (**a**) and sediment (**b**) of the Songhua River.

3.3. Ecological Risk Assessment

Aquatic organisms, including phytoplankton, zooplankton, invertebrates, fish, etc., live in aquatic environments; thus, they are closely related to the environmental water quality. The quotient approach was employed to assess the ecological risk of PAHs to aquatic organisms in the Songhua River, China. This approach has been previously used to determine the risk characteristics of organic compounds [45–47]. The hazard quotients (HQ) of PAHs were calculated as follows:

$$HQ = \frac{C_{\text{exposure}}}{TRV} \quad (12)$$

where $C_{exposure}$ is the environmental monitoring concentration of an individual PAH and TRV is the toxicity reference value of a PAH, which are presented in Table 2. Generally, HQ > 1.0 indicates that a PAH poses a potential threat to aquatic ecosystems, and HQ < 1.0 indicates that the risk is relatively low.

Table 2. Toxicity reference values of PAHs in freshwater and sediments.

PAHs	Water (µg/L)	Sediments (µg/g)
Acy	NA	NA
Ace	23	NA
Flu	11	0.077
Phe	30	0.042
Ant	0.3	0.057
FlA	6.16	0.111
Pyr	7	0.053
BaA	34.6	0.032
Chr	7	0.057
BbF	NA	NA
BkF	NA	NA
BaP	0.014	0.032
IcdP	NA	NA
DahA	5	0.033
BghiP	NA	NA
∑PAHs	NA	4

Note: NA: not available.

Figure 8 illustrates that the HQ values of individual PAHs in different seasons in the Songhua River were less than 1.0, except for Pyr in the sediment in spring. Additionally, the values of HQ are relatively low compared to those in other rivers in China, such as the Liaohe River and Jiulong River [47]. Thus, the ecological risk of PAHs to aquatic organisms in the Songhua River is relatively low.

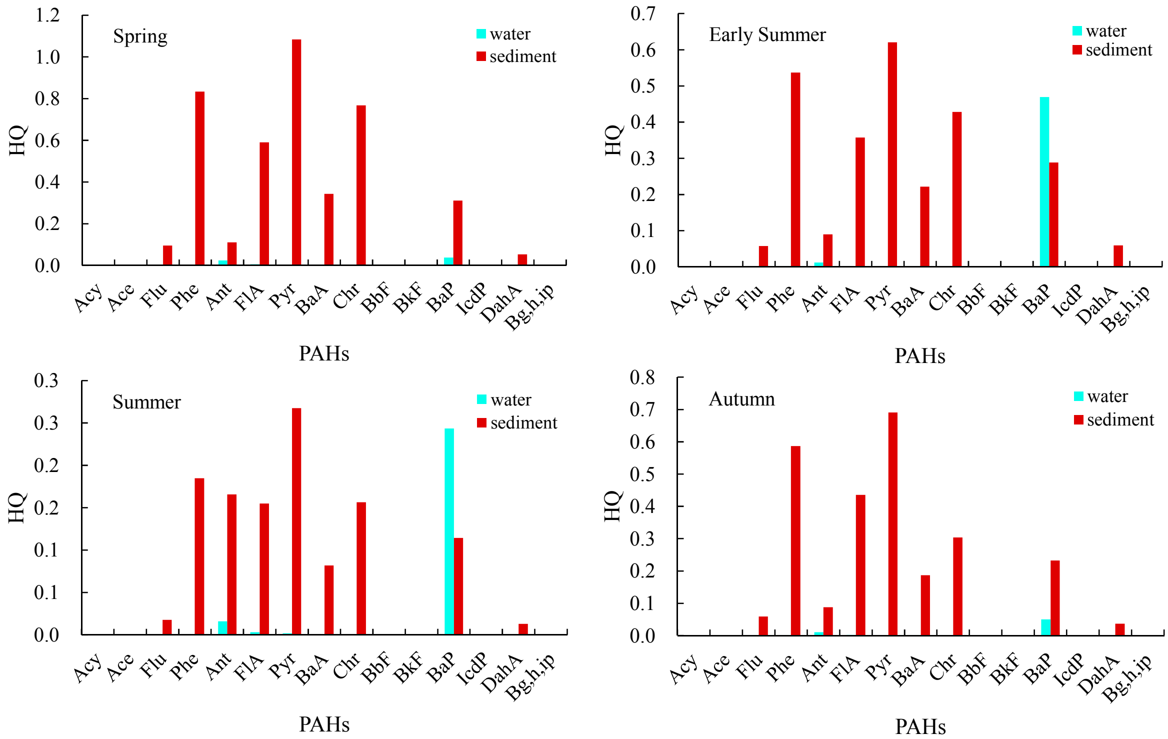

Figure 8. Hazard quotients of PAHs in different seasons.

4. Conclusions

The sediment–water exchange, spatial variations, and ecological risk in the Songhua River, China, were comprehensively investigated and explored in this study. The results showed that the sediment acts as a secondary emission source for three- and four-ring PAHs; however, five-ring PAHs are deposited in the sediment from the water. The high *ff* values of PAHs in autumn suggest a large release of PAHs after abundant deposition during the summer. The *ff* values of PAHs, especially those of five- and six-ring PAHs, were lowest in summer, reflecting deposition from the water to the sediment. The simplified qualitative method of $C_{water}/C_{sediment}$ is useful for assessing variations in the sediment–water exchange. The five-ring PAHs were more sensitive than three- and four-ring PAHs, resulting in straightforward exchange between the sediment and water. PAHs with high molecular weights in the water and sediment exhibits large variations compared to PAHs with low molecular weights. Additionally, the ecological risk of PAHs to aquatic organisms is relatively low in the Songhua River.

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