Behavior and fate of alkylphenols in surface water of the Jialu River, Henan Province, China

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Abstract

The behavior and fate of alkylphenols (APs) were studied in surface water from the Jialu River, Henan Province, China. Located at its upper stream, Zhengzhou city is regarded as the major discharge source to this river with its annual effluents containing 726 kg for nonylphenol (NP) and 30.2 kg for octylphenol (OP). The concentrations of NP and OP in surface water ranged from 75.2 to 1520 ng L\(^{-1}\) and from 20.9 to 63.2 ng L\(^{-1}\), respectively. To assess the behavior of APs along the river, a mass balance equation based on chloride was adopted, due to its relative conservation. The results showed that dilution effect was prevailing in determining the APs concentrations in surface water along the river. The effect of potential biodegradation was also estimated with an assumption of the optimized biodegradation. The contributions of dilution and biodegradation to the decline of APs concentrations were 38.8%, 23.7% for NP and 57.8%, 24.3% for OP, respectively. The other contribution to the decline of APs concentrations along the river was considered as an integrated effect of adsorption and air–water exchange with the values of 37.5% for NP and 17.9% for OP. The decay half-lives of NP and OP from surface water bodies were 1.6 and 2.4 d, respectively. About 70.2% of total NP and 24.1% of total OP were finally eliminated from water phase to surrounding matrix in the downstream. The results suggested that the downstream river channel served as the net sink of APs in the study area.

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1. Introduction

Non-ionic surfactant of alkylphenol ethoxylates (APEs) are widely used for industrial, domestic and commercial applications, such as lubricating oil additives, detergents and antistatic agents (Blackburn et al., 1999; Fenet et al., 2003). APEs are mainly composed of nonylphenol ethoxylates (NPEs) and octylphenol ethoxylates (OPEs), which account for about 80% and 20%, respectively (Keith et al., 2001; Sharma et al., 2009). Concern has increased about the relatively stable degradation products of APEs, alkylphenols (APs) such as nonylphenol (NP) and octylphenol (OP). APs have been classified as endocrine-disrupting chemicals (EDCs) because of their effects on the hormonal system of numerous organisms by competing with oestrogen for binding receptors (Gibble and Baer, 2003). Because of their disturbing behavior, APs as well as their ethoxylates have been phasing out in some developed countries and have been designated as priority substances in Water Frame European Directive (Cailleaud et al., 2007; Soares et al., 2008).

As demonstrated by a number of publications, occurrence of APs in environment is closely correlated with anthropogenic activities and many studies have been carried out to identify the occurrence and fate of these chemicals in sewage treatment plants (STPs) (Kannan et al., 2003; Céspedes et al., 2008; Ying et al., 2008), sediments (Chen et al., 2006; Fu et al., 2007), surface and ground water (Latorre et al., 2003; Li et al., 2004). In China, APs contaminations have been found in many rivers, lakes and estuaries with a wide variety of concentrations (Jin et al., 2004; Shen et al., 2005; Xu et al., 2006). Chen et al. (2006) reported that the concentrations of APs in surface water of the Pearl River Delta, ranged from <0.020 to 0.628 µg L\(^{-1}\) for NP and <0.002 to 0.068 µg L\(^{-1}\) for OP. Although some studies have reported the occurrence and fate of APs in aquatic environment, their environmental behavior such as dilution, diffusion, degradation and adsorption in natural water remain uncertain (Cailleaud et al., 2007).

The Huaihe River, one of the five main rivers in China, was seriously polluted by a succession of catastrophic pollution accidents since 1994 (Huang et al., 2004). Gao et al. (2008) reviewed the phenoic compounds pollution in surface water of China, and gave the average concentration of 2,4-dichlorophenol as 20.2 ng L\(^{-1}\) with a maximum value of 246.0 ng L\(^{-1}\) in surface water of the Huaihe...
River. With the economic growth and urban development, serious pollution of surface water is expected in the Huaihe River basin, where there has been no report on APs contaminations yet. In order to study APs contaminations in the surface water, the Jialu River, one of branches of the Huaihe River was chosen. The objectives of this paper are (1) to make clear the distribution of APs in the surface water of Jialu River; (2) to understand the hydrochemistry evolution of surface water and dilution effect on the variance of APs concentrations and (3) to discuss the environmental behavior and fate of APs along the river.

2. Materials and methods

2.1. Site description and sample collection

Originating from Xinmi County, Henan Province, the Jialu River is 256 km long with its basin area of 5896 km². It flows via Zhengzhou, Zhongmou, Weishi and Xihua then down into the Shaying River near Zhoukou city (Fig. 1). The average discharge of the Jialu River measured by a gauge station in Zhongmou was 15.11 m³ s⁻¹ in 2007. The Jialu River basin has been undergoing a rapid economic growth and urbanization, facing massive discharge of wastewater and declining surface water quality. Wang et al. (2004) investigated the organic contamination of drinking water sources in Henan province and found 18 widely existing organic pollutants, the priority substances listed by US EPA, in the Jialu River basin. Large numbers of treated and untreated sewage from the alongshore cities and villages were estimated to be 25124 × 10⁴ tons per year from 1996 to 1999, 81% of which were discharged from Zhengzhou city (Xiao et al., 1999). The Zhengzhou city has a long history for textile and metallurgy industries, and has been listed as one of the six most important industrial cities by “the development of central zones” stratagem of Chinese Government. In 2006, the total population of the city was 7.20 millions, of this 3.06 millions was non-agricultural population (Statistical Bureau of Zhengzhou city, 2007). Thus, it is reasonable to assume that the Zhengzhou city has a strong impact on the surface water quality of the Jialu River.

Fig. 1 shows map of study area where the Jiangang reservoir (S₁), located at 4.5 km upstream of Zhengzhou city, serves as the drinking water source for the city. Water samples were collected with pre-rinsed 2 L glass bottles at each site along the river in September 2007. After filtering through a prebaked 0.45 μm glass fiber membrane in situ, the samples were subsequently refrigerated and the extraction was performed within 24 h.

In addition, another 200 ml surface water was taken at each site to analyze the concentrations of Ca²⁺, K⁺, Mg²⁺, Na⁺, Cl⁻ and SO₄²⁻ by using ion chromatography (LC-10A, Shimadzu, Japan). HCO₃⁻ was measured by titration using 0.01 M H₂SO₄, and total dissolved solid (TDS) was calculated by summing up all major ions. The chemical analysis results were adopted only when the charge-balance error was within ±5%. Repeated measures of dissolved oxygen...
(DO) were performed in situ by portable meters (D-55, Horiba, Japan). The global positioning system (GPS) was used to locate the sampling sites.

2.2. Analytical procedure

All solvents used for sampling and analysis were HPLC grade. 4-tert-octylphenol was purchased from Wako Pure Chemical Industries (Japan), 4-nonylphenol (mixture of compounds with different isomers) was obtained from Tokyo Chemical Industry, Japan. Phenanthrene-d10 was purchased from AccuStandard, Inc (USA). All the glassware used for organic compounds analyses were baked for 4–5 h at 450 °C prior to use to remove organic contamination.

The method of pretreatment for water samples was based on previous reports (Isobe et al., 2001; Liu et al., 2004). Briefly, each filtrate was extracted by solid-phase extraction cartridge (InertSep RP-1, GL sciences). These cartridges had been previously washed with 5 ml each of dichloromethane, methanol, and ultrapure water. The analyte was eluted from cartridges with 20 ml dichloromethane after 30 min dryness, and then the solution was concentrated to 0.2 ml under a gentle stream of high purity nitrogen. An appropriate volume of the internal standard (phenanthrene-d10) was added into samples prior to GC–MS analysis. APs were analyzed by using Gas chromatography–mass spectrum (Shimadzu GC-2010, Shimadzu MS-Parvum2). An Rtx-5MS fused silica capillary column (30 m, 0.25 mm i.d., and 0.25 μm film thickness) was employed with helium as the carrier gas at a constant flow rate of 1 ml min−1. GC–MS operating conditions were 70 eV ionization potential and the electron multiplier voltage at 1100 eV.

Concentrations of NP and OP in surface water samples from the Jialu River were found in the range of 75.2–1520 ng L−1 for NP and 1.1 and 3.6 ng L−1 for OP, respectively. The recovery was checked through three replicate analyses of samples spiked with known levels of all target compounds (100 ng L−1). The spiked samples were then extracted and analyzed. The average recoveries of NP and OP were 89% and 81% and their relative standard deviation (RSD) were 8.4% and 6%, respectively. For every batch of ten samples, a solvent blank and a procedural blank were run in sequence to check contamination. And according to the results of procedural blank analysis (n = 3), there was no blank correction to be performed due to undetected amounts of NP and OP. Duplicate of each water sample was processed and repeated analyses of each concentrated sample were performed to further validate the results. A non-parametric Spearman rank R correlation test was performed (p < 0.05) to assess relationships between APs and environmental parameters with the SPSS 13.0 for windows.

3. Results and discussion

3.1. Occurrence of APs in surface water along the Jialu River

Concentrations of NP and OP in surface water samples from the Jialu River are shown in Fig. 2. Both NP and OP were detected in all water samples analyzed, at concentration above their respective LOQ. The concentrations of NP and OP in the Jialu River were found in the range of 75.2–1520 ng L−1 and 20.9–63.2 ng L−1, with mean values of 645 ng L−1 and 39.8 ng L−1, respectively. There was a significant positive correlation between NP and OP concentrations (R = 0.771, p < 0.05). This implies that the NP and OP were together released into the aquatic environment and probably underwent probably similar processes along the river (Watanabe et al., 2007). Both NP and OP have maximum concentrations at S2, about 2 km downstream of Zhengzhou urban zone, and then decreased along the river. However, the lowest concentrations of NP and OP were detected at S1, which was less influenced by human activities. As a result, the urban zone was generally considered to make great

Fig. 2. Concentrations of NP, OP and DO in the Jialu River in relation to distance from sampling site S1. Mean of repeated analyses was plotted with one standard deviation (repeated measures of DO concentration were performed in situ).
contribution to the increase of APs and Kolpin et al. (2004) also demonstrated a statistic greater ($p = 0.01$) levels of APs in samples collected from downstream than those collected upstream of urban centers in USA.

There were some reports on the concentrations of APs in river water from various locations in the world (Table 1). Sharma et al. (2009) also summarized the concentrations of NP and OP in river water from different regions of the world and reported a level of 0.006–32.8 $\mu$g L$^{-1}$ and $<0.001$–1.44 $\mu$g L$^{-1}$ for NP and OP, respectively. Thus, it was found that NP and OP concentrations in the Jialu River were similar to these results.

Renner (1997) reported that the lowest effect level of NP was 1.0 $\mu$g L$^{-1}$ in freshwater with a view to a safety factor of 0.1 in Europe, and 1.0 $\mu$g L$^{-1}$ was also considered as the threshold level of NP for fish vitellogenin stimulation. In addition, Japanese Ministry of the Environment gave no effect concentrations of 0.608 $\mu$g L$^{-1}$ for NP and 0.992 $\mu$g L$^{-1}$ for OP on fish, respectively (Ministry of the Environment of Japan, 2001; Watanabe et al., 2007). Based on these documents, the NP concentrations observed from S2 to S4 in this study exceeded the limit and might be potentially hazardous to fish, which therefore may be potential dietary exposure of human (Keith et al., 2001).

The aquatic toxicity assessment of EDCs has been commonly focused on the STPs effluents (Jobling et al., 1998; Kannan et al., 2003; Sumpter and Johnson, 2005). However, it seems that a longer distance (i.e. 10–100 km) should be taken into account when assessing the risk associated with these compounds (Williams et al., 2003).

The DO concentrations ranged from 0.53 to 6.1 mg L$^{-1}$ with the average concentration of 2.75 mg L$^{-1}$ in the river. The highest DO concentration was found at S1, where water quality was good with the lowest TDS value. Along the river, DO concentration decreased to the lowest at S3 and then increased gradually until 3.64 mg L$^{-1}$ at S6. DO had significant negative correlation with NP ($R = -0.943$, $p < 0.01$) and with OP ($R = -0.829$, $p < 0.05$). It was similar to the relationship of NP and DO reported in the Edogawa River (Watanabe et al., 2007). Some studies have reported that the APEs metabolites were completely degraded to APs only under anaerobic conditions (Giger et al., 1984; Ying et al., 2002). Thus, it can be concluded that it became more and more difficult for complete degradation of APEs to form APs owing to the increase of DO along the Jialu River.

3.2. Surface water evolution and chloride variances along the River

Chloride is regarded as a relatively conservative ion during the environmental transport. So it can be used as an indicator for determining the water movement under most circumstances (Panno et al., 2006). The origin of chloride is mainly from the rock weathering and discharges of industrial, agricultural and domestic wastewaters (Tang et al., 2003). Therefore, if the hydrogeological background is relatively the same along a river, the dramatic change of chloride concentration can be considered as the results from the anthropogenic influences or water dilution.

The relationship between the values of Na$^+$ and Cl$^-$ in surface water along the river is shown in Fig. 3. It was found that all data exclusive of S2 were plotted along the 1:1 line of molar Na$^+$/Cl$^-$ ratio. The result suggests that the river received a large amount of wastewaters containing numerous chlorides when it flowed through Zhengzhou city. The water types were also different from Ca–HCO$_3$ at S1 to Ca–Na–HCO$_3$–Cl at S2. There are three STPs in urban zone of Zhengzhou and their total treatment potencies are about $80 \times 10^4$ t d$^{-1}$. The treated water was finally discharged into the Jialu River and these effluents made up 46% of the Jialu river flow in 2006 (Lu et al., 2008). These effluents of STPs contained relatively high concentrations of Na$^+$ and Cl$^-$ according to the domestic usage and the technologies applied in wastewater treatment procedures (Marti et al., 2004; Panno et al., 2006). Relatively stable water chemical types (Ca–HCO$_3$) were found from S1 to S6 along the river, both Cl$^-$ and Na$^+$ concentrations decreased but the Na$^+$/Cl$^-$ ratio was almost the same. The results suggest that the surface water undergo similar evolution with no big chloride supplement after S2 and only dilution can be considered as a main physical process between S1 and S2. The effluent from interval between S1 and S2 constituted the major chloride and APs sources to the Jialu River.

3.3. Behavior of APs in surface water along the Jialu River

APs are both the raw materials and biodegradation products of APEs, and can enter natural water by a variety of pathways. A series of processes would happen including dilution, photolysis, biodegradation and sorption to suspended particulate matter (SPM) after APs enter into aquatic environment. Most APs entering the aquatic environment are highly water soluble with 40–80% of which are detected in the dissolved phase and 20–60% in SPM (Isobe et al., 2001; Li et al., 2004; Cailleaud et al., 2007). Thus, it is valid to suggest that hydrodynamics can play an important role in determining the fate and behavior of APs in river system (Jones et al., 2002; Williams et al., 2003; Sumpter and Johnson, 2005).

To understand the environmental behavior of APs in the Jialu River, it is necessary to estimate the dilution of surface water along

![Fig. 3. The relationship between Na$^+$ and Cl$^-$ along the Jialu River (→ represents direction of river flow from S1 to S6).](image-url)
the river. There is no major tributary along the Jialu River except the Shuangji River that is more depleted in Cl⁻ concentration with its little recharge to the Jialu River because of reservoirs located in its downstream. Thus, it is necessary to consider the total amount of chloride remain constant in the downstream after S₂. Percentage of water dilution at each sampling site was calculated by the mass balance of chloride, based on which the deduction equation below was used to estimate the theoretic APs concentrations along the river by just considering dilution effect:

\[
\text{Calculated } - \text{AP}(i) = \text{actual } - \text{AP} \times \frac{\text{Cl}_i}{\text{Cl}_1} (i = 2, 3, 4, 5)
\]

where \(\text{actual } - \text{AP}_i\) represents the factual concentrations of APs obtained by analysis at \(S_i\). \(\text{Calculated } - \text{AP}(i+1)\) is the calculated concentrations of APs at \(S_{i+1}\) under the consideration of only the dilution effect. \(\text{Cl}_i\) and \(\text{Cl}_1\) are the concentrations of chloride at \(S_i\) and \(S_1\), respectively. The dilution percentage was considered as 0 at \(S_2\). Furthermore, based on the above equation, the calculated-APs concentrations at \(S_0\) can be evaluated with the dilution ratio \(\frac{\text{Cl}_0}{\text{Cl}_i}\) and actual-AP\(_2\). The contributions of dilution effect to the decline of APs concentrations after \(S_2\) were estimated at 38.8% for NP and 57.8% for OP. Therefore, the result suggests that physical dilution is an important process to determine the concentrations of APs in the River.

The calculated concentrations of APs at each sampling site along the river are shown in Fig. 4. Differences between actual concentrations and calculated concentrations of APs represent the net results of degradation, air–water exchange and adsorption/desorption at the interval between sampling sites. The differences in the downstream were found to be larger than those in the upper stream, which indicates faster dissipation from water bodies have occurred along the river from the upper stream to the downstream. Interestingly, calculated NP concentrations had a relatively slight change while the actual NP concentrations showed a fast decline between \(S_3\) and \(S_4\). However, actual OP concentrations had a more modest change than calculated OP in this reach (Fig. 4). The explanation for the different behaviors between NP and OP might be due to their physical–chemical characteristics. It was reported that the octanol/water partition coefficients \((\log k_{ow})\) of NP is 4.48 and that of OP is 4.12 (Ahel and Giger, 1993). Difference in partitioning between NP and OP shows that NP should have higher affinity and is easily partitioned to SPM or sediment than OP, while OP can remain longer in water bodies than NP. Li et al. (2004) reported that NP in SPM varied by season and increased along the downstream water of Han River in all seasons, which was similar with the behavior of NP in water. And the partition coefficient \((\log k_W = 4.8)\) and the correlation \((R^2 = 0.63)\) for SPM phase and water phase clearly indicated that NP was readily adsorbed to SPM and rapidly reach the equilibrium between water and SPM. Liber et al. (1999) also demonstrated that once released into littoral zone of pond ecosystem, NP has a relatively short time in the water column but more persistent in sediment. And the short persistence in water column was apparently not a result of degradation but rather largely a sequence of the hydrophobic nature of NP leading to a partitioning to solid.

According to average width of the Jialu River and its average flux 21.68 m² s⁻¹ during the sampling period, the calculated flow velocity of the river was 49.9 km d⁻¹. That is, about 3.0 d were required for the effluent to flow down from \(S_2\) to \(S_6\). Ying et al. (2003) simulated the aerobic degradation of NP and OP in seawater and found their half-lives to be 5 and 60 d, respectively. Staple et al. (2001) reported that ultimate biodegradation half-lives of NP and OP were 8.2 and 12.4 d at 22 °C in the laboratory, respectively. Because there are many chemical and environmental factors which influence biodegradation of APs in the field, the laboratory biodegradation rates have a bias with actual biodegradation in aquatic environment. However, to assess the potential biodegradation of APs in the Jialu River, the extent of optimized biodegradation of APs was evaluated on the basis of the above document (Staple et al., 2001). The results show that about 23.7% and 24.3% of total decrease in NP and OP concentrations were caused by biodegradation in the Jialu River.

The adsorption, air–water exchange and photolysis of APs are also important processes in controlling their fate in aquatic system. The photolysis rate in the deeper layers was strongly attenuated being about 1.5 times slower at depths of 20–25 cm than at the surface (Ahel et al., 1994). In consideration of the practical sampling depth (>20 cm) and the low water transparency of polluted river water, the direct photolysis of APs below the surface layer was negligible in the Jialu River. Johnson et al. (1998) showed that the SPM adsorbed 5–35 times more OP than respective bed sediments based on the carbon-for-carbon basis in Aire and Calder rivers, which indicated that the SPM may play a key role in determining the fate of OP. Cailleaud et al. (2007) reported that NP to be the major APs compound measured in the SPM and represents 66.9 ± 9% of total APs in SPM. In addition to dilution and biodegradation, the adsorption of SPM may be the other important process in determining the behavior of APs along the river. The Henry’s Law constant for NP was estimated at 3–4 × 10⁻⁸ atm m² mol⁻¹, which are sufficient to support air–water exchange of APs to the atmosphere (Dachs et al., 1999). Therefore, taking air–water exchange and adsorption into consideration, their integrated effect on the decline of NP and OP concentrations from \(S_2\) and \(S_6\) were estimated at 37.5% and 17.9%, respectively.

![Fig. 4. Comparison of calculated-APs and actual-APs concentrations in surface water along the Jialu River. (a) NP (left); (b) OP (right).](image-url)
3.4. Fate of APs in surface water along the Jialu River

The ratio of NP/OP can be used to determine the environmental fate within a river and the ratio value of 3–5 has been reported in surface water (Latorre et al., 2003). In the present study, the ratio of 3.35 at S1 was considered as a background value, and it dramatically increased to 22.5 at S2. After S2, a fast decline process was found until the ratio fell back to 3.6 at S6. The results also imply that the NP performed a more effective elimination from water body than OP along the Jialu River.

The water body of each interval between adjacent sampling sites can be regarded as a compartment (S(i+1)−i). The net inflow and outflow of APs in each compartment can be estimated based on the following equations:

\[ F_i = C_i \times Q_i \quad (i = 2, 3, 4, 5) \]  
\[ F_o = C_{i+1} \times Q_{i+1} \quad (i = 2, 3, 4, 5) \]

where \( F_i \) and \( F_o \) are the inflow and outflow of APs at sites \( S_i \) or \( S_{i+1} \), respectively; \( Q_i \) and \( Q_{i+1} \) are the discharge of river water at \( S_i \) and \( S_{i+1} \), respectively. \( C_i \) and \( C_{i+1} \) represent the concentrations of APs at \( S_i \) and \( S_{i+1} \), respectively. Furthermore, the amount of optimized biodegradation can also be evaluated based on certain assumptions. The typical first order die-away kinetics and optimized rate constants of ultimate biodegradation were listed as Eqs. (4) and (5).

To assess the ultimate potential biodegradation of APs in the Jialu River, the pseudo-first order half-lives of APs were obtained by extrapolating the laboratory results (Staple et al., 2001).

\[ C_t = C_o e^{-kt} \]  
\[ k = \ln \frac{2}{t_{1/2}} \]

where \( k \) is pseudo-first order rate constant, \( C_o \) and \( C_t \) are the concentrations of APs at time 0 and \( t \), respectively. \( t_{1/2} \) is half-life of APs. \( t \) is time which can be estimated by the flow velocity of the river. Thus, the ultimate potential biodegradation amounts of each compartment were calculated as 38.5–147 g d\(^{-1}\) for NP and 2.77–4.50 g d\(^{-1}\) for OP, respectively. In fact, the biodegradation of APs in the Jialu River would be lower than the estimated values because of the low DO levels and microbial population in the river.

The fate of APs in each compartment was evaluated using the mass balance concept:

\[ F_i = F_o + F_d + A \]

where \( F_d \) is ultimate biodegradation amount of APs in each compartment. \( A \) represent the integrated effects of adsorption/desorption and evaporation/deposition. The physical significance of \( A \) represents the direction of mass transfer between water body (dissolved phase) and surrounding matrix in the river. In this study, the positive numbers suggest the water body serves as supplier and exports material to surrounding matrix. The negative numbers represent the contrary (Fig. 5). The sum of \( A \) (\( \sum A \)) of NP at upper stream compartments \( S_{3-2} \) and \( S_{4-3} \) was 8.41 g d\(^{-1}\) while it was 1396 g d\(^{-1}\) at downstream suggesting the dramatic declining of NP from water bodies occurred in the downstream. Similar to NP, the analysis results of \( \sum A \) for OP indicate a break-even mass transfer in the upper stream and almost all elimination of OP from water bodies to surrounding matrix occurred in the downstream. As a result, the downstream of the Jialu River serves as net sink of APs to the upper stream. It was also found that the ratio of \( \sum A \) and \( F_i \) at \( S_2 \) can be used to the ultimate fate of APs in the whole river. The ratios of \( \sum A/F_i \) were 70.2% for NP and 24.1% for OP, indicating that about 70.2% of NP and 24.1% of OP were finally released from water body to surrounding matrix in the river.

As shown in Fig. 5, the assessments also indicate that the inputs of APs from the Zhengzhou urban zone were 726 kg per year for NP and 30.2 kg per year for OP, respectively. Liber et al. (1999) assessed the persistence and distribution of NP in an experimental littoral ecosystem and found a dissipation half-life of ≤1.2 d in water body. In this study, the half-lives of decay from surface water bodies were 1.6 and 2.4 d for OP and OP, respectively. The concentrations of APs in reservoir water of \( S_1 \), which appeared to be the lowest, can be regarded as the background values in the Jialu River basin. The total storage of NP and OP at the reservoir was 0.79 kg and 0.27 kg, respectively. However, the daily output of NP from Zhengzhou urban zone was two times larger than the total background storage at the reservoir. Thus, the intensive human activities from Zhengzhou urban zone supplied huge APs pollutants to the aquatic ecosystem of the Jialu River.

4. Conclusions

The endocrine-disrupting chemicals NP and OP were detected at relatively high levels in surface water of the Jialu River. The lowest and highest concentrations of these compounds were found in the upper stream and downstream of Zhengzhou urban zone, respectively. The significant NP concentrations (about 1.0 μg L\(^{-1}\)) in surface water remain until about 70 km downstream of the urban zone. Thus, Zhengzhou city can be regarded as the main discharging source of APs to the downstream, and the annual discharges of NP and OP from its urban zone to the river were 726 kg and 30.2 kg, respectively.

Based on the mass balance equation of chloride, the dilution effects of river were calculated to estimate the behavior of APs along the river. Dilution’s contribution to the declines of NP and OP concentrations between \( S_0 \) and \( S_1 \) were 38.8% and 57.8%, respectively. According to published studies on the ultimate biodegradation of APs, biodegradation seemed to only play a subsidiary role in determining their fates in the river. On the basis of mass balance considerations, the fate of APs in each compartment was calculated and integrated effect \( A \) indicated the relation of water bodies and surrounding matrix. The elimination of APs from surface water bodies mainly occurred in the downstream of the river, where about 70.2%
of total NP and 24.1% of total OP were eliminated from water bodies to surrounding matrix. The results also indicate that downstream acted as the net sink of NP and OP toward the upper stream.

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