Journal of Environmental Management 293 (2021) 112953

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Transport and fate of antibiotics in a typical aqua-agricultural catchment explained by rainfall events: Implications for catchment management

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A R T I C L E I N F O

Keywords:
Emerging contaminants
Suspended particles
Diffuse pollution
Nutrients
Agriculture

A B S T R A C T

Antibiotics receive many concerns since their negative environmental impacts are being revealed, especially in aqua-agricultural areas. Rainfall events are responsible for transferring excess contaminants to receiving waters. However, the understanding of antibiotics transport and fate responding to rainfall events was constrained by limited event-based data and lacking integrated consideration of dissolved and particulate forms. We developed an intensive monitoring strategy to capture responses of fourteen antibiotics to different types of rainfall events and inter-event low flow periods. Pollutant-rich suspended particles, as high as 1471 ng/g, were found in low flow periods while the very heavy rainfall events and consecutive rainfall events stimulated the release of antibiotics from eroded soil particles to river water. Therefore, these rainfall events drove radical increase of dissolved antibiotic concentration up to 592 ng/L and total flux up to 25.0 g/d. Sulfonamides were particularly sensitive to rainfall events because of their residues in manure-applied agricultural lands. Transport dynamics of most antibiotics were accretion whereas only clarithromycin exhibited a dilution pattern by concentration-discharge relationships. Aquaculture ponds were inferred to significantly contribute tetracycline, oxytetracycline, and clarithromycin. Conventional contaminants were compared to discriminate potential sources of antibiotics and imply effective catchment management. The results provided novel insights into event-based drivers and dynamics of antibiotics and could lead to appropriate management strategy.

1. Introduction

Emerging contaminants are transported in different environmental compartments, in which non-prescription drugs, pesticides, and antibiotics have the highest detection degrees in surface waters (Focazio et al., 2008; Fairbairn et al., 2015). Antibiotics recently receive growing concerns because they are used globally for human beings or livestock, poultry, and aquaculture industries to prevent or treat diseases. Many studies have reported that antibiotics are ubiquitous in lotic (e.g., streams and rivers) (Zheng et al., 2012; Bernot et al., 2013; He et al., 2016; Zhou et al., 2016) and lentic (e.g., lakes and reservoirs) water bodies (Zhou et al., 2016; Liu et al., 2018; Wang et al., 2018). These antibiotic residues changed microbial activities and functions (Sanderson et al., 2004; Blackwell et al., 2009), then have a detrimental impact (e.g., antibiotic resistance) on non-target organisms through prolonged exposure (Carusso et al., 2018).

Agricultural lands and aquaculture ponds are the main sources of antibiotic pollution in catchments (Seiler and Berendonk, 2012). A large proportion of antibiotics cannot be absorbed or metabolized in the human or animal body (Zhang et al., 2015a). Agricultural fields often received excrements from humans or animals as organic fertilizers (Zhao et al., 2020). Manure application brings antibiotics in soil environments, especially in agricultural lands which would export antibiotics by runoff and soil erosion (Zhao et al., 2020). The detection level of tetracyclines (TCs) antibiotics was found to increase by manure application (Dong et al., 2019). The use of antibiotics as feed additives and medicines is also common and extensive in aquaculture ponds (Chen et al., 2018). Sulfonamides (SMs) were the most prevalent antibiotics detected in the monitored aquaculture ponds in southern Taiwan (Lai et al., 2018). A higher detected concentration of antibiotics in aquaculture ponds than

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https://doi.org/10.1016/j.jenvman.2021.112953
Received 3 March 2021; Received in revised form 22 May 2021; Accepted 28 May 2021
Available online 5 June 2021

surrounding streams or canals was found (Lai et al., 2018; Wang et al., 2018). However, there is little information on antibiotic transport mechanisms from source to environment due to the complexity of nonpoint source pollution pathways.

The role of rainfall events on contaminant transport was widely discussed for conventional pollutants such as nutrients and suspended particles (SPS) from diffuse sources (Sherriff et al., 2016; Xie et al., 2019a). Surface runoff driven by intense rainfall events probably mobilizes substantial excess nutrients, degrading the quality of receiving water bodies. However, very few studies focus on the variability of antibiotic behaviors caused by rainfall events. The majority of the relative research is focused on seasonal variation of antibiotic occurrences and concentrations (Bailey et al., 2015; Tang et al., 2015; Dong et al., 2019; Lu et al., 2020). Higher detection rates and concentrations of antibiotics during and after the rainy season were found by Kim et al. (2016), which were attributed to the role of rainfall-runoff on antibiotic concentrations. Previous studies usually conducted minimal sampling campaigns that were likely not fully representative of the wide-ranging characteristics of rainfall events and thereby limited the understanding of event-based behaviors of antibiotics (Mijangos et al., 2018). Besides that, eroded particles carried antibiotics to rivers as contaminated SPS during rainfall events, however, the important role of these SPS in source-sink behaviors of antibiotics was rarely discussed (Zhou et al., 2013; Dong et al., 2019).

The purpose of this study was to explore the impact of rainfall events on the transport and fate of antibiotics in a typical aqua-agriculture catchment which locates in the lower region of the Yangtze River Basin, China. Fourteen frequently used antibiotics were measured by an intensive monitoring regime including event-based samplings. The specific aims were to (i) clarify how rainfall events and inter-event periods impacted the antibiotic behaviors in both river water and SPS; (ii) characterize antibiotic concentration-discharge relationships to determine transport dynamics and drivers from hydrologic pressures and aqua-agricultural activities; (iii) discuss similarities and disparities between conventional and emerging contaminants in their responses to rainfall events to select appropriate management strategies.

2. Materials and methods

2.1. Chemicals and reagents

Preliminary investigation indicated that SMs, fluoroquinolones (QNs), macrolides (MLs), and TCs are the typical antibiotics used in aquaculture. Therefore, fourteen antibiotics including three TCs (tetracycline (TC), oxytetracycline (OTC), and chlorotetracycline (CTC)), three QNs (ciprofloxacin (CIP), ofloxacin (OFL), and enrofloxacin (ENR)), three MLs (roxithromycin (ROX), azithromycin (AZI), and clarithromycin (CLA)), and five SMs (sulfamethoxazole (SMX),

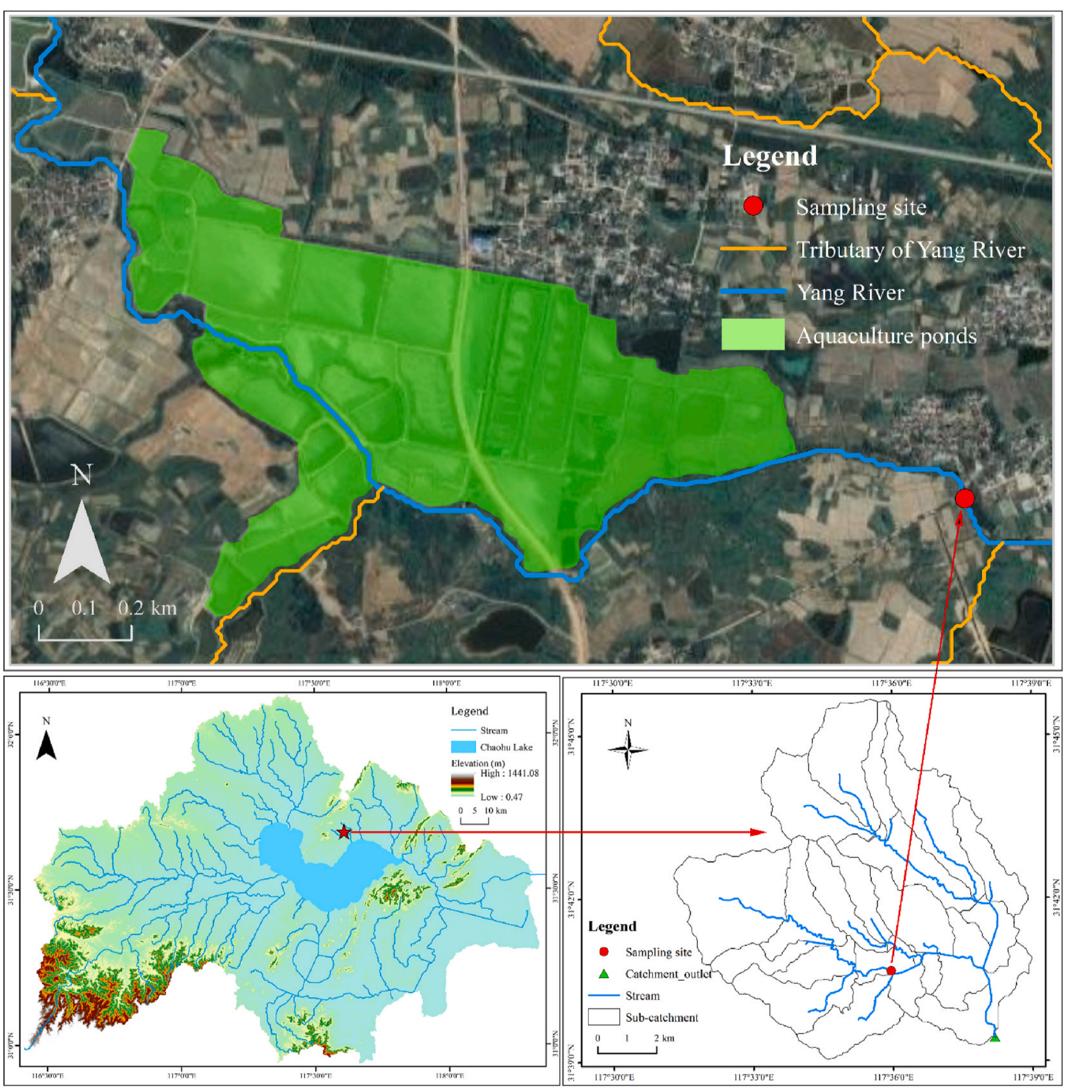

Fig. 1. Location of the sampling site, the aqua-agriculture catchment, and the Chaohu Lake.

sulfadimidine (SDM), sulfadiazine (SDZ), sulfamerazine (SMZ), and sulphacetamide (SPT)) were obtained from Merck & Co., Inc. (Darmstadt, Germany). The physico-chemical properties of the studied antibiotics are listed in Table S1 in supporting information (SI). The internal standard (^{13}C3-caffeine) was supplied by J&K Scientific Ltd. (New Haven, C.T., USA), as well as HPLC grade methanol, formic acid (≥98%, Aladdin), and acetonitrile. Ethylenedinitrilotetraacetic acid disodium salt (Na_2EDTA) and hydrochloric acid (HCl) were analytical reagents. All glassware was pre-cleaned as described in our previous study (Dong et al., 2019).

2.2. Site description and sampling strategy

The Chaohu Lake is situated at the lower Yangtze River basin in China. It is the fifth largest shallow freshwater lake, whereas it is exceptionally polluted by antibiotics (Tang et al., 2015). Our study site is located at its north shore in the Tongyang catchment (Fig. 1). The catchment area is 89.3 km^2. Tong River and Yang River are the two main streams that converge near the outlet and enter directly into the Chaohu Lake. Agricultural land covers about 60.4% of the total area. Around 9.3% of the Tongyang catchment is covered by farm ponds, most of which are exploited for aquaculture (e.g., crayfish and shrimp) while the proportion is still growing. The agriculture and aquaculture bring a lot of anthropogenic pressures with nonpoint source pollution on the terrestrial and aquatic environments in this catchment.

The sampling site is in the middle of the Yang River (Fig. 1). A crayfish breeding center comprised of aquaculture ponds of 0.36 km^2 is close (about 380 m upstream) to the sampling site. Paddy fields are also adjacent to the sampling site. An intensive monitoring campaign was designed (as shown in Fig. 2a) and implemented to elucidate the impact of rainfall events on the transport and fate of conventional and emerging contaminants. Our measurements started on 25th April and ended on August 28, 2019. During this period, the accumulated precipitation amounts to 58.9% of the annual total precipitation. According to the local weather forecast, water samples were collected post-event and inter-event to capture how these contaminants behaved as responded to different types of rainfall events as well as dry periods between events. The detailed sampling regime was presented in Fig. 2. Standard methods issued by the Ministry of Ecology and Environment of China were followed to measure concentrations of ammonia (NH_4–N), nitrate

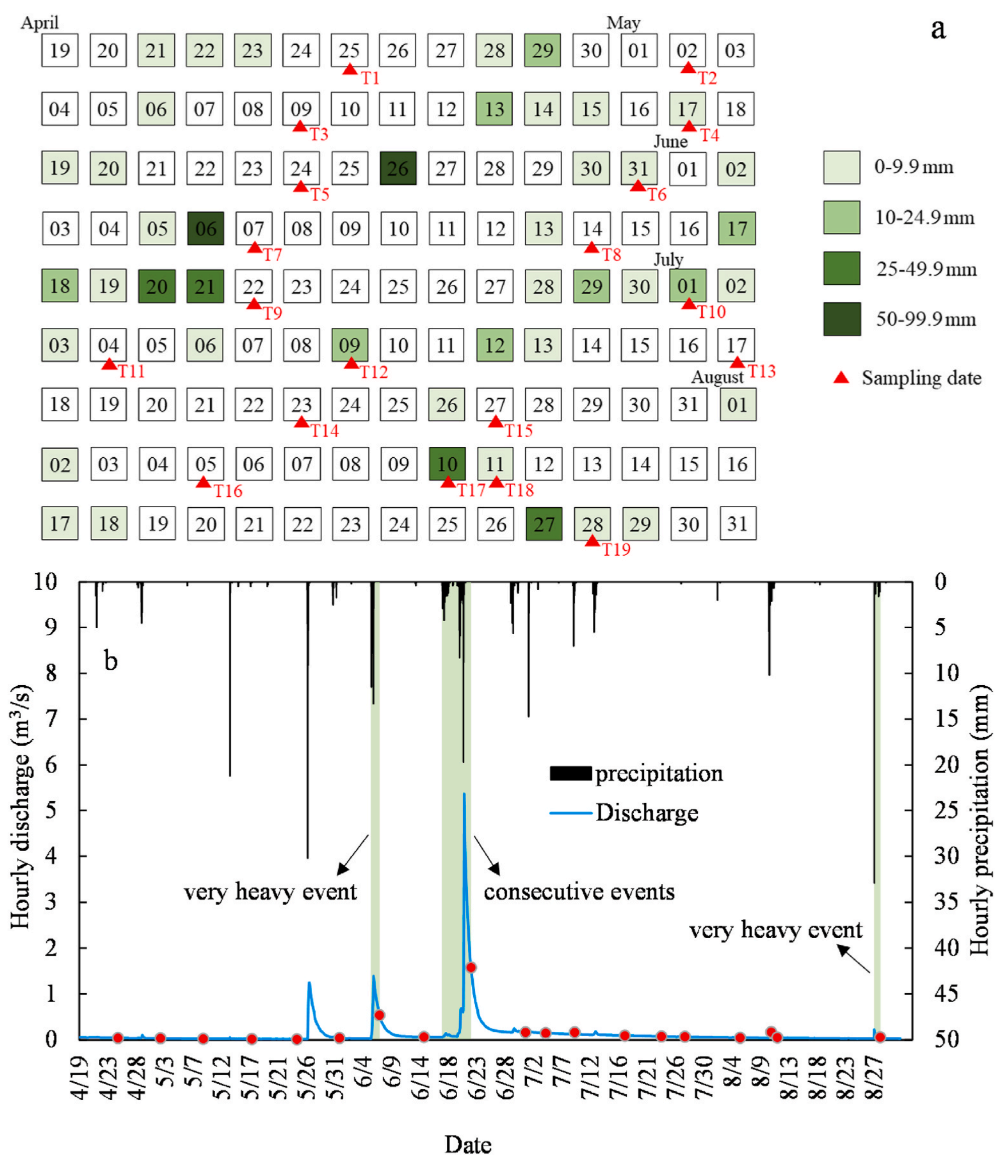

Fig. 2. Sampling time, precipitation, and discharge. Fig. 2a shows the daily rainfall amounts and the sampling dates and numbers (T1-T19). Fig. 2b shows the hourly hydrograph, hyetograph, and the sampling time. Red dots represented the sampling times corresponded to the discharge. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

(NO_3–N), nitrite (NO_2–N), phosphate (PO_4–P), total nitrogen (TN), and total phosphorus (TP) in surface water.

2.3. Analysis of antibiotics in overlying water and SPS

Water samples (3 L) were collected at 20 cm below the river water surface in the center of river cross section with a water sampler, and in-situ filtered through pre-weighed 0.45-μm glass fiber membranes to obtain the SPS samples. All samples were stored in 4 °C and transported to the lab as soon as possible. The detailed extraction processes of antibiotics in water and SPS were described in SI 1.1 and can be found elsewhere (Dong et al., 2019).

2.4. Measurement of antibiotics

The measurement of antibiotics was determined with ultra-performance liquid chromatography-tandem mass spectrometry (U-HPLC-MS/MS, Thermo, USA) with Q-Exactive Orbitrap™ detector (Thermo, USA). An ACQUITY UPLC BEH C_{18} column (100 mm × 1.0 μm) was used as the analytical column at a flow rate of 0.30 mL/min. Mobile phase A is formic acid solution (0.1%) in Milli-Q ultrapure water, and mobile phase B is the formic acid solution (0.1%) in acetonitrile. The gradient conditions are set as follows: 0 min, 95%A; 8.00 min, 95%B; 9.00 min, 5%A; 9.10 min, 95%A; 12.00 min, 95%A. The column temperature was 35 °C. The ejection volume was 10 μL. The MS was set in positive electrospray ionization (ESI+) mode for detection and identification of the targeted antibiotics. The optimized operation conditions of the MS were described in our previous studies (Dong et al., 2019) and summarized in SI 1.2.

2.5. Quality assurance/quality control

The coefficient of determination for all the standard curves was higher than 0.99. The method detection limit (MDL) for antibiotics ranged from 0.02 to 2.0 ng/L, which was calculated using six duplicates of blank samples according to the International Union of Pure and Applied Chemistry (IUPAC) method (MDL = mean+3SD). The concentrations of antibiotics in the lab blank samples were below the limits of detection. All the samples were in triplicate, and the results are expressed as average ± standard deviation (ng/L for dissolved antibiotics and ng/g for particulate antibiotics). The recoveries of spiking each antibiotic in water (10 ng/L, 50 ng/L, and 200 ng/L) and SPS samples (20 ng/g, 100 ng/g, and 400 ng/g) were 87.7%–102.4% and 68.3%–105.2%, respectively.

2.6. Statistical analysis

Individual rainfall event was extracted from the time series of hourly precipitation data by inter-event time (i.e., rainless intervals exceeding a defined duration), which was chosen as 2 h in this study (Gaál et al., 2014). Events with rainfall amount no more than 0.1 mm were excluded. Classification of rainfall events was based on the method (Table S2) commonly used in China (Xie et al., 2019b).

A power-law function ($C = a \times Q^b$, where C and Q were pollutant concentration and discharge, a and b were empirical coefficients) was used to investigate transport dynamics of emerging contaminants (Kibuye et al., 2020). The slopes (b values) of logarithmic C-Q plots classified contaminant transport patterns as dilution ($b < 0$), accretion ($b > 0$), or chemostatic ($b \approx 0$) (Vogel et al., 2005). Coefficients of variation for contaminant concentration (CV_C) and discharge (CV_Q) were calculated, while the ratio of the two CV values (CV_C/CV_Q) was used as a nonparametric measure to discriminate chemostatic behavior. The CV ratio<0.3 represented chemostatic dynamics, while the ratio>0.3 indicated a relatively larger pulse of contaminant exceeded over discharge variability (Thompson et al., 2011).

The risk quotients (RQs) method is a prevalent method to assess the environmental risks of antibiotics to aquatic organisms (EC, 2003). RQs values for algae, invertebrate, and fish were estimated as follows:

$$RQ = \frac{MEC}{PNEC} \tag{1}$$

$$PNEC = \frac{LC_{50}}{AF} \tag{2}$$

where *MEC* and *PNEC* are the measured environmental concentration and the predicted no-effect concentration of each antibiotic, respectively; LC_{50} is the half lethal concentration listed in Table S3; *AF* is the assessment factor to be 1000. Estimated RQs were used to categorize risk levels into three levels: high (RQ ≥ 1), medium (0.1 ≤ RQ < 1), and low risks (RQ < 0.1).

3. Results

3.1. Rainfall events, discharges and SPS concentrations

The rainfall amounts to approximately 60% of the annual total precipitation during the monitoring period. A total of 31 rainfall events consisting of 16 light events, 3 medium events, 8 heavy events, and 4 very heavy events were included. The water samples were collected for these different kinds of rainfall events as well as for low flow periods that were inter-event intervals. Stream discharges at the sampling site were simulated by the calibrated hydrologic model detailed in SI 1.3. As shown in Fig. 2, the very heavy events on 6th June and 21st June caused the increases of discharge to 1.39 m^3/s and 5.36 m^3/s, respectively. This marked difference was due to consecutive rainfall events occurring during 17th-20th June which wetted soils to a more saturated condition thereby resulted in runoff generation on T9 to a larger extent than on T7. The very heavy event on 27th August, however, just led to a rise of discharge to be only 0.22 m^3/s. The main reason was the over 7-day antecedent dry period which offset the driving force of the event to generate adequate runoff. During the sampling period, the average observed SPS concentrations were 36.7 ± 34.8 mg/L while the maximum value (122.0 mg/L) was observed on T17 when a heavy rainfall event lasted for more than 24 h and antecedent dry days were 8 days. SPS concentration on T7 was also particularly high due to the very heavy event. Medium and light rainfall events played a much less important role in increasing discharge and SPS concentration. Characteristics of the discussed rainfall events were presented in Table S4.

3.2. Event-based variation of antibiotics in river water and SPS

Eight of fourteen target antibiotics were found in river water samples, including three SMs, two TCs, two MLs, and one QNs (Fig. 3 and Fig. S3). The mean concentrations of antibiotics in river water showed a sequence of SMs (113 ng/L) > TCs (85.7 ng/L) > QNs (24.9 ng/L) > MLs (6.68 ng/L). The detection frequencies of SDZ, SMX, SPT, ROX, and CLA were higher than those of OFL, TC and OTC. SMX was detected in all samples while the maximum concentration was 524 ng/L on the sampling event T7. SPT, SDZ, and CLA were also ubiquitous as their detection frequencies were 50% and mean concentrations were 12.0, 58.1, and 17.4 ng/L, respectively. SDZ only occurred during May–June. The occurrences of MLs (ROX and CLA) were focused on the period from July to August, and the QNs (OFL) were detected during May. The concentrations of TC and OTC were as high as 55.5 and 148 ng/L, though they were only detected in two sampling events. MLs and QNs were sensitive to consecutive rainfall events during 17th-21st June.

Ten out of 14 antibiotics, including four SMs, two TCs, two MLs, and two QNs, were detected in SPS samples (Fig. 4). The concentrations of the total antibiotics were in the range of 4.36–1471 ng/g. The order of the antibiotic concentration averages in SPS was TCs (167 ng/g) > QNs (83.8 ng/g) > SMs (12.7 ng/g) > MLs (0.88 ng/g). SMX was detected in all SPS samplings with the highest concentrations of 25.8 ng/g. ROX,

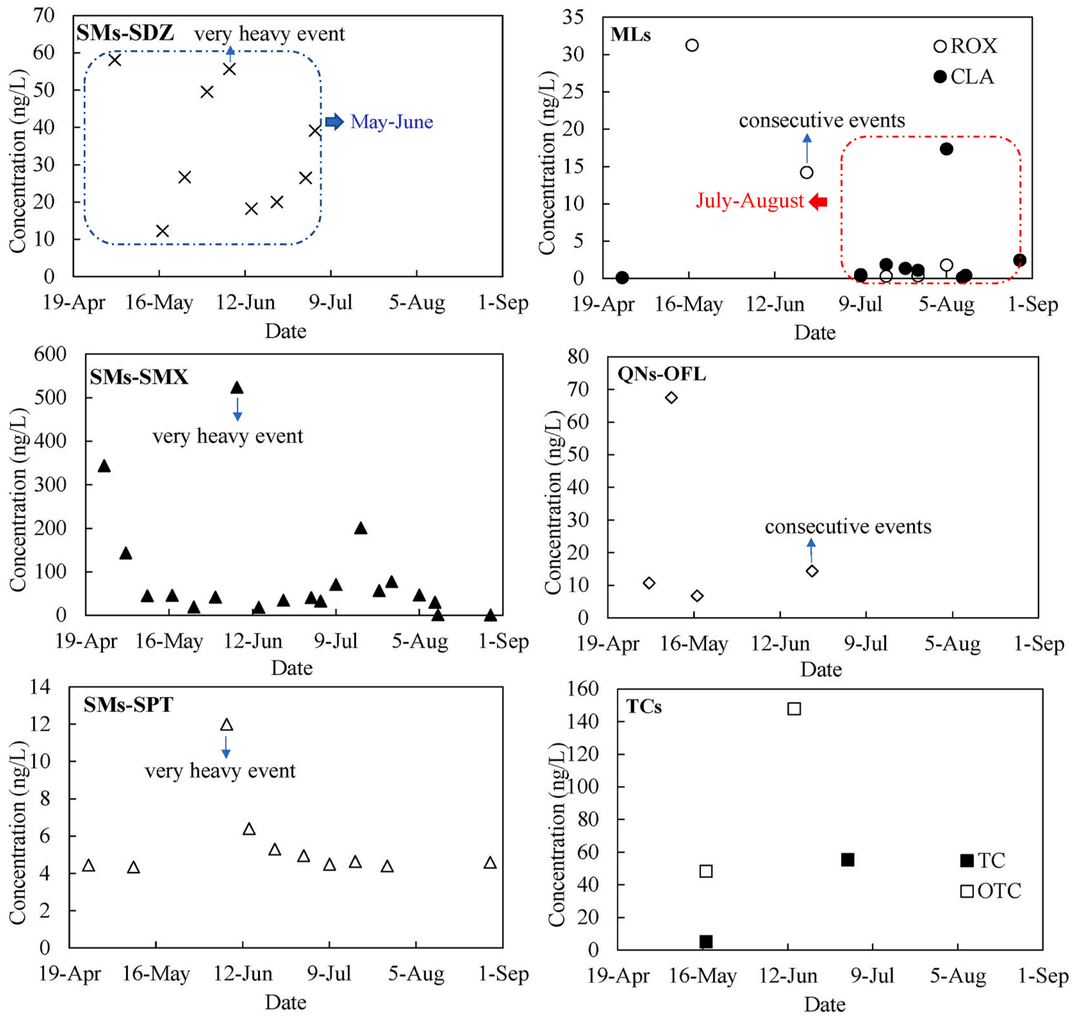

Fig. 3. Variations of the detected antibiotics in river water during the entire period.

CLA, and OFL were also ubiquitous, with detection frequencies of 80% and mean concentrations of 0.73, 0.25, and 82.8 ng/g, respectively. The detection frequency of OTC was 36%, with the maximum concentration of 894 ng/g. SDM and ENR were detected in SPS samplings whereas they failed to reach the detection threshold in the corresponding water samples. The partitioning coefficient (K_P, L/Kg) of antibiotics is a ratio of antibiotic concentration in SPS (C_S, ng/g) and the corresponding concentration in river water (C_W, ng/L). The log K_P values ranged from 1.37 to 3.57. The sequence of log K_P values for antibiotics was OFL > CLA > OTC > SPT > SMX > TC > SDZ > ROX.

C-Q relationships (Fig. 5) were investigated here for an improve understanding of transport dynamics of dissolved antibiotics. Accretion dynamics for SMX and ROX were obviously observed. CLA concentrations were decreased with the increase of discharges. No strong *C-Q* relationship was found for SDZ. The lowest CV_C/CV_Q ratio of SDZ suggested that its transport was the least influenced by concentration variability since its concentrations remained relatively constant in both low and high flow periods. OFL exhibited a weak *C-Q* relationship ($|b| = 0.04$) and a high CV ratio ($CV_C/CV_Q = 0.60$), implying the dominance of flow variability in its transport dynamics (Thompson et al., 2011).

3.3. Event-based variation of conventional pollutants

Variations of TN and TP concentrations and their compositions during the sampling period were presented in Fig. S4. Dissolved nitrogen was the dominant state of TN in river water and its proportion was 84.4 ± 19.9%. Conversely, the dissolved phosphorus only took up 43.3% of TP on average. The sampling event T7 was specifically mentioned here because of the extremely high concentrations of TN and TP ($p < 0.05$) compared to the ranges and low standard deviations of the observations on the other sampling events. The very heavy rainfall event on 6th June was right before the sampling event T7. This rainfall event lasted 13 h with an average rainfall intensity of 4.3 mm/h and the maximum rainfall intensity of 13.3 mm/h. The antecedent 7-day rainfall amount of this event was only 2.9 mm. The combination of these rainfall-related characteristics led to a radical increase in concentration of some nutrient species. It was also worth noting that the particulate state absolutely dominated the forms of the detected nutrients on T7. Absorbed nitrogen and phosphorus accounted to 81.8% and 96.7% of the TN and TP, respectively, which can be explained by the particularly high corresponding SPS concentration. Nutrient concentrations on T9 were quite insensitive as responded to the very heavy rainfall event on 21st June though the discharge was significantly large. The reason might be that consecutive events before the sampling event flushed considerably nutrient mass in soil pools. As for the *C-Q* relationships in Fig. 5, accretion dynamics ($b > 0$) was observed for most cases (NO_2–N, NO_3–N, PO_4–P, TN, and TP) as their concentrations increased with the increased discharges driven by rainfall events. NH_4–N showed a relation curve of thoroughly contrast direction which meant a dilution response ($b < 0$).

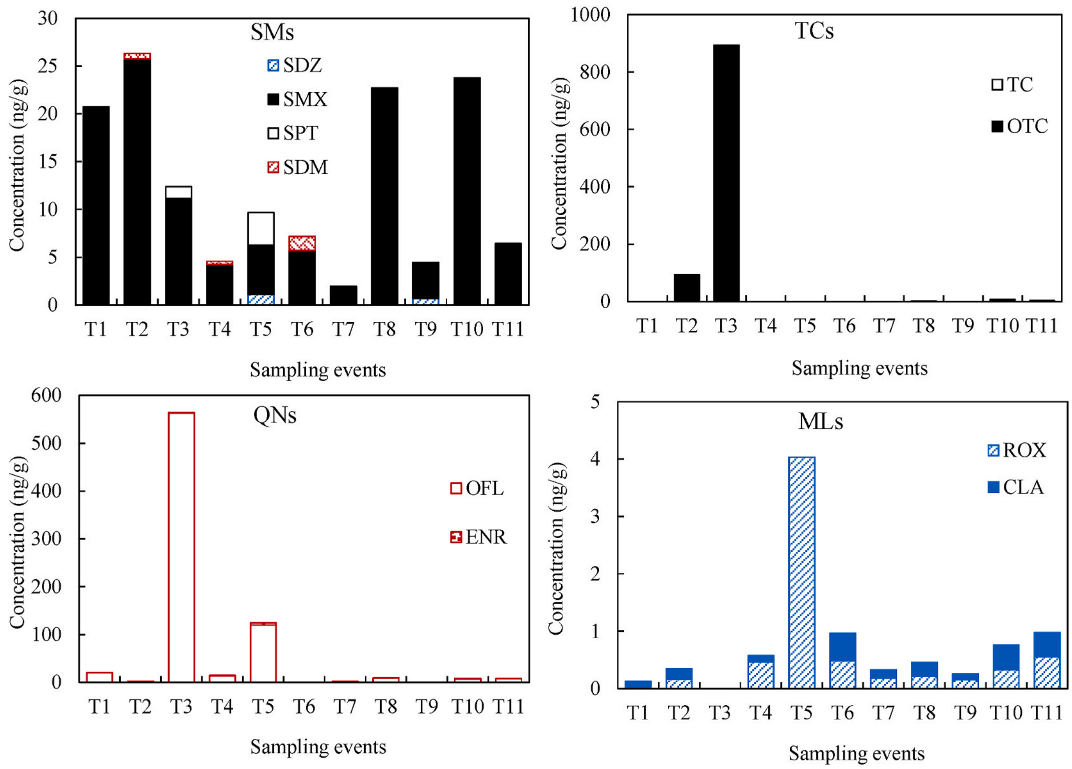

Fig. 4. Distribution of different antibiotics in suspended particles (SMs: sulfonamides; TCs: tetracyclines; QNs: fluoroquinolones; MLs: macrolides).

3.4. *Event-based assessment of antibiotic environmental risks*

Fig. 6 shows the risks to algae on different sampling events. Table S3 lists the highest risks to three different trophic levels (i.e., algae, invertebrate, and fish). All the detected antibiotics in river water represented low risks to invertebrates and fish. The RQs of SPT for all sampling events were lower than 0.1 due to its low toxicity ($E(L)C_{50}$ = 4730 mg/L, Li et al., 2014) and lower detected concentrations. SMX on T1, T7, and T13 had medium risks to algae. High risk of OFL to algae was found for T3. Furthermore, all detected OFL showed medium or high risks to algae, suggesting its deleterious effects on some aquatic organisms.

4. Discussion

4.1. *Importance of event-based monitoring of antibiotics*

Current monitoring of emerging contaminants was usually based on samplings of low temporal frequencies (e.g., monthly and seasonal) (Tang et al., 2015; Lu et al., 2020). Although this kind of monitoring was considered previously for occurrence characteristics, it is insufficient to depict short-term dynamics and often missed transit changes of concentrations and fluxes induced by specific rainfall events. From a practical point of view, it would bring uncertainty and biases and increase risks in decision making. Few studies have been concerned with the impact of rainfall events on the transport of antibiotics. Kim et al. (2010) designed a simulated rainfall event to address how antibiotics responded as diffuse pollution on the plot scale. Aqueous and sediment samples were taken every 5 min during the simulated event to capture the complete response curve of veterinary antibiotics. Such frequent sampling was not easy to follow in the reality where rainfall events are however random in occurrence and magnitude. The short-term scale might also be too short to represent the biochemical reaction and transport processes of antibiotics in a catchment scale. Monitoring procedures should be adapted to meet the nature of rainfall events and their potentially severe impact.

In this study, the sampling strategy designed herein covered the impact of different types of rainfall events as well as inter-event low flow periods. The combination of post-event and inter-event monitoring offered the opportunity to capture how the transport of different antibiotics fluctuated in a long-term period but with a sequence of different types of rainfall events included. Two very heavy rainfall events as potential drivers to cause severe pollution were targeted while their post-event impact on antibiotic transport was evaluated based on the two sampling events T7 and T9. Measurement results of SMs (the highest SMX and SPT concentrations and the second highest SDZ concentration) in river water on T7 indicated the mobilization of substantial antibiotic residues triggered by the very heavy rainfall event. Antecedent 5-day accumulative rainfall amount before this rainfall event was only 0.2 mm, which provided an opportunity for antibiotic accumulation. Such intense rainfall events are likely to accentuate over most areas as predicted by research about climate change (Besmer et al., 2017). Their significant impact on the transport and fate of antibiotics in aqua-agricultural catchments was to be expected based on our results. SMs concentrations in river water on T9 were 6 times lower than those on T7 (Fig. 3) although a very heavy event just happened before T9, mainly because continuous flushing by other antecedent events rapidly depleted many antibiotic residues, which caused a strong dilution effect of runoff (Shimizu et al., 2013). Results on T9 can be regarded as a representative evidence of the importance of consecutive rainfall events. Although SMs concentrations did not show a clear change on T9, the antibiotic flux (11.0 g/d) has increased dramatically due to the particularly high discharge compared to the average flux (0.64 $\pm$ 0.54 g/d) by other event types (Fig. S5). From the perspective of concentration and flux, our results confirmed the importance of event-based antibiotic monitoring to capture the pollution episodes and their adverse impact driven by rainfall events.

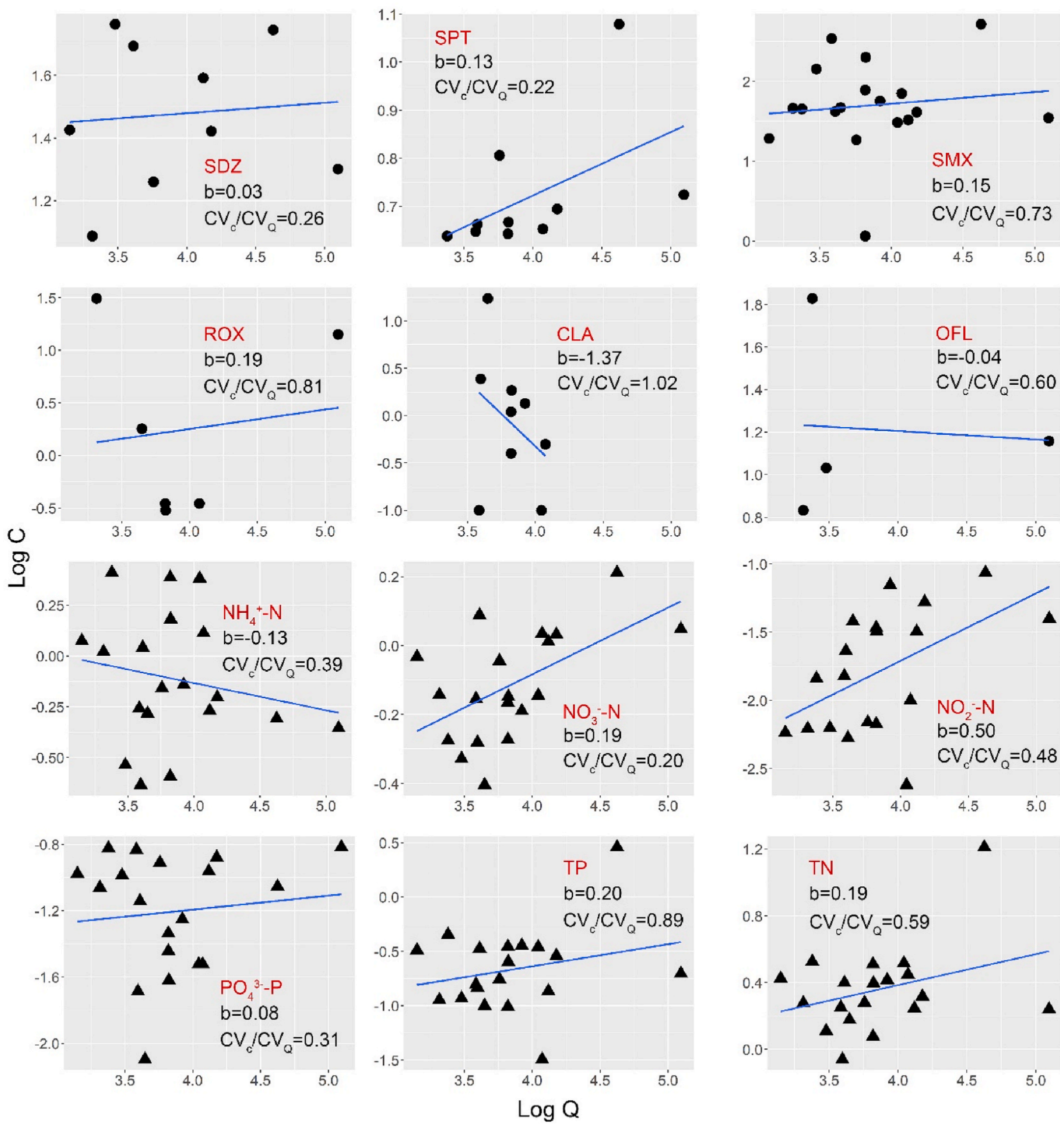

Fig. 5. Concentration-discharge (*C-Q*) relationships of antibiotics and conventional pollutants.

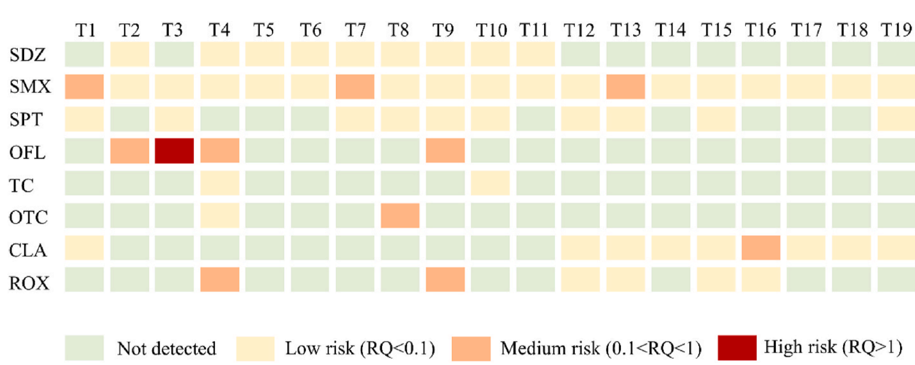

Fig. 6. Risk quotients (RQs) of detected antibiotics to algae for each sampling.

4.2. Impact of rainfall events on antibiotic transport

As discussed before, the very heavy rainfall event and consecutive rainfall events substantially increased the post-event SMs presence in the form of either dissolved concentration or flux. This conclusion corresponded to several previous research (Dong et al., 2019; Hitchcock, 2020) in which intense rainfall events severely impacted water quality in terms of emerging contaminants. Event-based characteristics (e.g., event duration, antecedent condition, rainfall intensity) were also important (Xie et al., 2019a). As shown in Fig. 3 and Fig. S3, a heavy event right before T17 did not result in high dissolved antibiotic concentrations as expected. It could be explained by the long antecedent low flow period thereby majority of the net precipitation infiltrated to moisten the soils and runoff response was rather inadequate to drive diffuse pollution with antibiotic transport (Corada-Fernández et al., 2017).

Monitoring during extremely dry periods between rainfall events was also necessary for the deduction of the potential sources and background levels of antibiotics export. Accumulative 5-day rainfall amounts before the sampling events T3 and T5 were under 1.0 mm; meanwhile, no rainfall events occurred 24 h before the two events, which represented typical dry periods. The source of the detected antibiotics during low flow periods excluded diffuse pollution processes driven by rainfall events. Given the hydrological connectivity between the aquaculture ponds and the sampled stretch of the reach, it might be inferred that detected SMX, SPT, OFL, and CLA on the extremely dry periods were likely from the aquaculture ponds to which antibiotics were applied. The total antibiotic concentrations in SPS on T3 and T5 were exceptionally higher (1471 and 138.2 ng/g) than those on other sampling events (Fig. 4). SPS may act as a sink of antibiotics during low flow periods. It was also worth noting that the total antibiotic concentrations in SPS on T7 and T9 were particularly low (<5 ng/g), which indicated the driving force of intense rainfall events for the release of antibiotics from eroded soil particles to river water.

Analysis of antibiotic categorization (Fig. 3) showed that their presence and transport were subject to anthropogenic pressures. All SMs on T7 responded radically to the typical extreme event ($p < 0.05$), indicating their diffuse sources from the surrounding agricultural fields. OFL and ROX mainly detected in May and July–August, respectively. They were both detected after consecutive rainfall events. TCs and QNs presented a stronger sorption to particles and sediments in soil-water systems than SMs (Figueroa-Diva et al., 2010), allowing higher detections of SMs in river water and higher concentrations of TCs and QNs in SPS. The maximum antibiotic concentration in SPS was 894 ng/g for OTC which was substantially high while dissolved OTC was not detected in the corresponding water sample. Moreover, particle-associated antibiotics were proven to persist in their original state for longer than dissolved antibiotics, which indicated antibiotics could accumulated on SPS and impact the environments in a long term of years (Kümmerer, 2009; Bailey et al., 2015). The commonly used environmental risk assessment method (e.g., RQ calculation) for antibiotics was targeted to their aqueous concentrations, the potential risks posed from antibiotics in SPS were scarcely known. Suspended particles can be eaten by many aquatic organisms (e.g., *Daphnia magna*) (Zhang et al., 2015b). Such a high level of antibiotic concentration is to be expected to cause risks for aquaculture and human beings.

The transport behavior of antibiotics in river water in response to discharge fluctuation driven by rainfall-events was further explored by *C-Q* relationships (Fig. 5). CLA presented a clear trend of dilution dynamics. It was detected only during July–August when stream discharges were relatively low. Its concentrations in river water were higher during non-event periods and decreased with the increasing of discharge by rainfall events. It was worth noting that the CV ratio>1, suggesting the relative variability of dissolved CLA concentrations exceeded that of stream flows. CLA behaved much like a point source pollutant (probably from aquaculture ponds by drainpipes) exporting mass input to the surrounding river water while the signal of natural fluctuations such as rainfall events would result in dilution effects rather than introducing more mass input from diffuse sources. Wang et al. (2018) also reported the significant role of aquaculture ponds in contributing antibiotic pollution in other areas in China and the phenomenon that CLA concentrations were decreased during wet seasons. The slope of *C-Q* relationship for SDZ was near zero ($b = 0.03$) while the CV ratio was smaller than 0.3, which is a representative of near-chemostatic behavior, that is its transport was barely impacted by rainfall events. SMX implied an accretion pattern ($b > 0$) because SMX concentrations increased with the elevated discharges. The CV ratio of SMX was as high as 0.73 which meant the relative variability of SMX concentrations was comparable to the discharge variability. These phenomena implied the dominant transport pathway of SMX into receiving waters was probably surface runoff which carried nonpoint source antibiotics from manure-applied agricultural fields (Zhao et al., 2020).

4.3. Comparison of transport dynamics between antibiotics and conventional pollutants

In general, diffuse pollution by excess sediment and nutrient is strongly affected by hydrologic processes and is therefore sensitive to rainfall events (Dai et al., 2019). In this study, the responses of emerging contaminants to the heavy rainfall events presented similarities with that of conventional pollutants. The maximum concentration of NO_2–N, NO_3–N, TN, TP, and SMX appeared simultaneously on T7. As responded on T9, both the conventional diffuse pollutants and antibiotics did not show a clear change in their concentrations though stream discharge was dramatically increased. Influencing factors such as continuous flushing process by the antecedent consecutive events, variation of pollutant sources, biodegradation rates or potential sorption may interact (Bernot et al., 2013). Throughout the entire sampling period, the transport dynamics for the above pollutants all showed accretion patterns for their *C-Q* relationships while NH_4–N and CLA presented dilution patterns conversely, implying their similar pollution sources (e.g., manure-applied lands and aquaculture ponds, respectively) and transport pathways (e.g., runoff and erosion that resulted in the mobilization of pollutants, and drainage by aquaculture activities, respectively).

The increase of nutrients was dominated by particulate states (Fig. S4) due to the corresponding high SPS concentrations, whereas the increase of antibiotics in river water on T7 were attributed to the release of antibiotics from SPS. This could be proved by the evidence that the total antibiotics concentrations in SPS on T7 are as low as 4.36 ng/g, over 20 times lower than the average levels in SPS. The results obtained from our previous research also indicated that the increase of TCs in river water was resulted from the release of antibiotics from SPS during transport caused by intense rainfall events, highlighting the important role of SPS in antibiotic transport and fate (Dong et al., 2019).

4.4. Implications for catchment management

Many previous studies have found high frequencies and high exports of antibiotics during wet seasons (Tang et al., 2015; Lu et al., 2020). However, wet seasons consist of individual rainfall events and inter-event dry periods, to which how antibiotics responded was still a challenge to understand. This knowledge gap is mainly due to the negligence of the impact of rainfall events and the paucity of event-based data. Based on this motivation, we would argue that rainfall events should assume immediate attention to understanding the transport and fate of antibiotics. Antibiotics export and transport in this aqua-agricultural catchment was also tied closely to rainfall events based on our results. The highest detected SMX concentration (524 ng/L) influenced by the very heavy rainfall event was around ten times as much as the concentrations during long-term low flow periods. Exceptionally low concentrations SMX occurred on T19 mainly because a heavy rainfall event right before was likely to wash away large amount SMX residues. Seasonal or monthly sampling and analysis used by previous studies might underestimate the pulse signals of radical fluctuation caused by rainfall events, which causes the underestimation of environmental risks and brings uncertainty to management strategies accordingly.

Transport patterns of antibiotics showed similarities and disparities compared to conventional diffuse pollutants. Best management practices (BMPs) aimed at mitigating excess nutrients could also bring benefits to controlling some antibiotics emissions. Limiting the use of manure is one of the commonly used managerial BMP for diffuse pollution (Sun et al., 2020), which would definitely reduce antibiotic losses to receiving waters since manures usually contain antibiotics for human and veterinary use and are a major contribution to antibiotic residues in soil (Sun et al., 2017; Zhao et al., 2020). Given previous research (Xiong et al., 2015; Dong et al., 2019) and our results, detention-based BMPs (e.g., grassed waterways and detention ponds) receiving agricultural runoff would be efficient in intercepting and retaining not only nutrients but also antibiotics. If these kinds of BMPs are planned to implement, practitioners will not have to alter or purchase any surplus equipment for antibiotic control. There was also evidence to prove differences of transport dynamics between diffuse nutrients and antibiotics. TC and OTC were only detected in three sampling events in May and June. Our field surveys confirmed the deduction that TCs primarily came from aquaculture ponds. Crayfishes easily got sick during May and June when TCs were concentratedly applied in the pond waters, thereby it was not surprising that TCs were occasionally detected with high concentrations in both river water and SPS.

The Chaohu Lake has been suffering from antibiotic stress, which also poses threats to the aquatic environment of the Yangtze River (Liu et al., 2018). Tang et al. (2015) studied eight inflowing rivers of the Chaohu Lake and suggested that urbanized catchments with wastewater effluents contributed a great portion of antibiotic pollution. The Tongyang catchment is another inflowing catchment where the highest detected SMX, SDM, OTC, and TC concentrations were exponentially higher than the other eight inflowing rivers. Since aquaculture ponds are distinctive landscapes not only surrounding the Chaohu Lake but also in the middle and lower region of the Yangtze River Basins (Song et al., 2016; Wang et al., 2018), our results highlighted the need to address more attention to aquaculture ponds as significant sources of antibiotics pollution (Chen et al., 2015; Zhang et al., 2018). A 10-year fishing ban for mainstreams, tributaries, and large lakes and reservoirs in the Yangtze River Basin was announced on January 1st, 2020 by the government in China. Given that the strict policy would cause the booming of aquaculture to meet the demand of aquatic products, more paddy fields and irrigation ponds are probably to be turned into aquaculture ponds in the near future. Freshwaters polluted by aquaculture ponds under intense hydrologic and anthropogenic pressures would address more severe environmental risks from antibiotic emission on aquatic organisms.

In future research, more targeted monitoring campaigns will be designed and optimized to reflect a comprehensive pathway for antibiotic transport and fate. Evidence of SPS being a significant source for antibiotics release was found. Further in-depth studies will be carried out to investigate the underlying mechanisms and quantify the potentially high environmental risks of SPS.

5. Conclusion

This study highlighted the importance of rainfall events on the transport and fate of antibiotics in water-SPS systems. Based on the intensive sampling regime, results showed that the very heavy rainfall events and consecutive events could radically increase antibiotic export and transport in terms of concentration and flux, indicating the rainfall-induced mobilization of substantial antibiotic residues by diffuse pollution. The potentially high environmental risks of antibiotics in SPS to aquatic organisms were neglected to some extent. SPS should receive particular consideration because of the antibiotic accumulation to SPS during low flow periods whereas the release from SPS to river water driven by intense rainfall events. The *C-Q* relationships revealed that the dominant transport pathway of SMX into receiving waters was probably surface runoff which carried antibiotics from manure-applied agricultural fields. Dilution patterns for both NH_4–N and CLA implied similar pollution sources and transport pathways. BMPs related to limiting manure application and increasing sedimentation would also be effective for antibiotic controls. Generally, the impact of rainfall events on the transport and fate of antibiotics in this typical aqua-agricultural catchment was of great importance jointly with anthropogenic pressures.

Credit author statement

Hui Xie and Jianwei Dong wrote the manuscript. Hui Xie designed the sampling strategy and conducted field sampling. Jianwei Dong conceived the study, funded the research, and carried out the laboratory experiment. Xinghui Xia revised the manuscript. Ranran Feng, Xijun Lai, Hongtao Duan, and Ligang Xu supported the sampling and laboratory experiment.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

We are grateful to all anonymous editors and reviewers for providing comments on this paper. We also appreciate the generous financial support provided by the National Natural Science Foundation of China (No. 51809177, No. 51909166, and No. 42007362), the Major Science and Technology Program for Water Pollution Control and Treatment, China (No. 2017ZX07603001), and the Talent Start-up Project of Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences (No. Y8SL031001).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2021.112953.

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