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Field migration of veterinary antibiotics via surface runoff from chicken-raising orchard in responding to natural rainfalls

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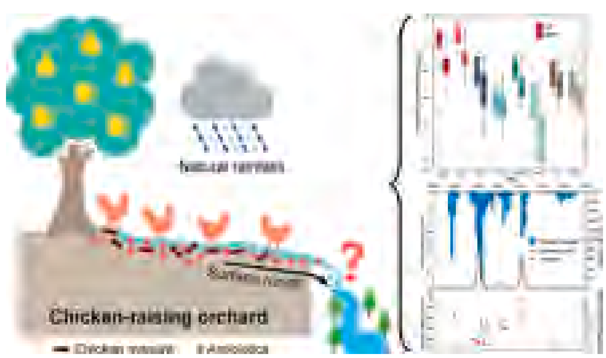
HIGHLIGHTS

- Dynamics of antibiotic concentration responded obviously to the rainfall intensity.
- Migration of sulfonamides and florfenicol higher than quinolones and tetracyclines
- Free-range chicken raising significantly increased antibiotics migration in surface runoff.
- Antibiotics correlated with variation of manure DOM fluorescence during rainfalls.
- Fluorescence indices can be used as a tracer based on antibiotics-manure DOM interactions.

GRAPHICAL ABSTRACT



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ABSTRACT

Knowledge on runoff transport of manure-sourced antibiotics from farmland soil to aquatic environment is limited due to complexity of hydrological regime and pathways. This study monitored natural rainfalls in sloping orchard plots with free-range chickens, with an attempt to investigate the migration characteristics of typical antibiotics via surface runoff as well as the impact of manure presence. Results showed that rainstorms continuously carried away antibiotics in surface runoff and all target antibiotics including those with high affinities to soil were detected at the beginning of runoff production. Concentration of antibiotics was found to respond strongly to the instantaneous rainfall intensity, showing consistent fluctuations during rainfalls. Concentrations of sulfonamides and florfenicol were two orders of magnitude higher than that of tetracyclines and fluoroquinolones. Compared to the control without raising chickens, antibiotics migration was considerably increased with the increased runoff production due to soil surface changes caused by chicken activities. Additionally, dynamics of antibiotic concentration significantly correlated with variations of fluorescent DOM components. Chicken manure-derived DOM mainly contained tryptophan moiety, and laboratory fluorescence

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quenching test with 2D-COS analysis indicated that all antibiotics interacted more strongly and preferentially with tryptophan than humic-like species. Antibiotics bonded to manure DOM with an affinity corresponding to the significance level of their correlations. In this light, potential use of fluorescence indices based on the established correlations may provide a convenient tool for tracing runoff migration of antibiotics during rainfalls.

1. Introduction

Veterinary antibiotics are usually used in animal husbandry to treat or prevent animal diseases (Kuppusamy et al., 2018). As emerging organic contaminants, however, their ubiquity in soil and water environment has attracted global attention due to potential risk referred to antibiotic resistance transmission (Danner et al., 2019; Liu et al., 2022). An important source for the entry of antibiotics to the environment is application of manure and slurry as additional fertility supply in farmland soils (Zhao et al., 2020). Extensive studies have reported antibiotic residues in poultry and livestock excreta such as chicken and pig manure, leaving farmlands a hotspot of non-point antibiotic contamination (Ho and Ho, 2012; Martinez-Carballo et al., 2007). According to the Veterinary International Committee on Harmonization (VICH), antibiotics >100 μg/kg in soil can trigger eco-toxicity (Shi et al., 2014), and the risk may spread to the surrounding environment via rainfalls.

The transport of antibiotics from terrestrial to aquatic systems depends primarily on the hydrological regime of the region (Kim et al., 2016). For instance, hilly topography and soil erosion result in increased risk of contaminant transmission in the vast area of southwest China where farmlands are highly prone to storm runoff (Gbadegesin et al., 2022; Xian et al., 2018). In the field, on a smaller scale, the soil provides hydrological paths for antibiotics migration either via surface runoff or leaching through soil pores (Gbadegesin et al., 2022; Zhang et al., 2022a). Up to now, several studies have investigated runoff transport of antibiotics from manure-fertilized farmlands under rainfalls, while information on real-time migration during a rainfall process is very limited. Besides, manure effect on surface soil and runoff production is also unclear. It was found out, method of manure application and time before rainfall would affect antibiotics level in surface runoff (Le et al., 2018). Presence of manure was reported to increase the antibiotics transport (Kulesza et al., 2016). Runoff migration of contaminants is greatly influenced by rainfall conditions including duration and intensity (Kim et al., 2016; Pan and Chu, 2017). Storm or extreme rainfall events are key moments for contamination in aquatic environment (Corada-Fernan De et al., 2017; Hitchcock, 2020). At lab scale, many column studies have been conducted with simulated rainfalls, the migration characteristics obtained from the breakthrough curves are, however, cannot image the actual scenario of contaminant transport in the field.

Additionally, antibiotics can migrate in association with suspended particles and colloids, leading to enhanced transport (Zou and Zheng, 2013; Kulesza et al., 2016). Some antibiotics are found to have high adsorption potentials for colloidal particles between 1 nm and 10 μm in diameter (McCarthy and Zachara, 1989). Dissolved organic matter (DOM), a pool of mobile and reactive organic colloids in the hydrosphere, has been recognized as critically important in affecting the transport of organic contaminants (Mohanram et al., 2012; Pelley and Tufenkji, 2008). Apart from the ubiquitous soil-sourced colloids, DOM can also be derived from excretion and food debris of poultry and livestock that are applied as organic fertilizer for soil amendment (Kivits et al., 2018; Zhou et al., 2016). Manure substrate-derived DOM has been reported to perform as a mobilizing agent for soluble contaminants (Hall et al., 2020; Kim et al., 2016; Pan and Chu, 2017). By characterization using fluorescence quenching tests and other spectroscopic technologies, solid results have demonstrated that DOM contains certain functional groups that interact with antibiotics, and antibiotics are inclined to bind non-covalently with protein-like substances rather than other moieties (Zhang et al., 2022b; Yan et al., 2016; Zhang et al., 2019). Certainly, such interactions vary among antibiotics of different molecular characteristics, leading to different impacts on their dispersion and migration in soil (Ferrie et al., 2017; Wang et al., 2015; Yan et al., 2016). With the help of two-dimensional correlation spectroscopy (2D-COS), the interaction mechanisms are able to be probed at molecular scale by analyzing specific sequences of spectral intensity changes (Noda, 2016).

So far, occurrence of antibiotics in rivers and watersheds has been reported to correlate strongly with the DOM fingerprint, as expressed using optical indices such as the relative intensity for the humic-like component, the a(250)/a(365) value, the normalized maximum fluorescence intensity (F_{max}/DOC), etc. (Stedmon and Bro, 2008; Zhang et al., 2019; Zhou et al., 2016). In this light, application of these established correlations may provide a convenient tool for monitoring the trace-level contaminants as well as for source apportionment. During rainfall processes, however, the feasibility for the method to trace antibiotics through runoff migration remains unclear.

Sloping farmland of an Entisol commonly called as purple soil, which accounts for 85 % of the basin area of Sichuan, China, is the most important agricultural land resource in the upper reaches of the Yangtze River (Xian et al., 2018). The soil is low in organic matter and poorly aggregated thus vulnerable to water erosion and easy for contaminants migration (Zhang et al., 2016). In this study, chicken-raising orchard plots were selected in the area with an attempt to investigate the migration of several veterinary antibiotics via runoff process in the field. Continuous monitoring of rainfall events was carried out in the rainy season and surface runoff samples were collected for antibiotics determination and DOM characterization. Laboratory quenching experiment was also conducted using multiple spectroscopic techniques. The objectives are: (1) to observe the dynamics of antibiotic concentrations in the surface runoff responding to natural rainfalls; (2) to investigate the influence of chicken manure on the field-scale migration of antibiotics; (3) to find potential antibiotic-manure DOM correlations and to understand the underlying mechanism in exploring the feasibility of using spectroscopic indices to trace the runoff migration of antibiotics during rainfalls.

2. Material and methods

2.1. Study area, field experimental setup and rainfall monitoring

The orchard field was located at Sichuan Yanting Agro-ecosystem Research Station of Chinese Ecosystem Research Network (CERN), Mianyang, China (31°16′N, 105°28′E). The site is a hilly agricultural catchment and the region has a moderate subtropical monsoon climate with a mean annual temperature and precipitation of 17.3 °C and 826 mm, respectively. The soil in the area is classified as an Entisol (according to the USDA Taxonomy). The soil is widely distributed in the southwest China, covering a total area of 160,000 km^2. The soil in the orchard field was made up of 30 % sand, 46 % silt and 24 % clay, respectively, with a pH value of 7.98 and an organic carbon content of 1.57 %. Detailed soil properties were shown in Tables S1–S2.

During over ten years preceding our experiments, the field has been cultivated with shaddock (*Citrus maxima (Burm.) Merr.*). Free-range chickens are raised under the fruit trees (at a density of 1250 chickens per hectare), which has been practiced as a popular ecological farming model in rural China. Two treatments were carried out in this study: Two parallel plots with chicken raising (manure-fertilized plot, MFP) and one control plot without chicken (CP). Three adjacent experimental plots were built in a local farmer's orchard (167.86 and 66.11 m^2 for MFP1 and MFP2, and 132.27 m^2 for CP, respectively). The whole filed was 6° in slope. As shown in Fig. 1, the plots were equipped with a self-made monitoring system, including stainless steel walls to hydrologically isolate external water recharge (30 cm underground and 20 cm above ground), flume at the end of the sloping plot and tanks to collect surface runoff samples, automatic tipping buckets (UA-003-64, HOBO, USA) to estimate the flux and rain gauges to count rainfall amount.

With manure discharge by free-range chickens on soil surface in the field (equivalent to 10 g/m^2 fresh matter per day), eight target antibiotics were applied at 0.0375 g/m^2 in each plot based on assessment of manure production and the recommended antibiotic dosage. Solution of antibiotics was manually sprayed to guarantee a uniform spatial distribution. This application is to illustrate a contamination scenario from manure fertilization according to poultry farming practice under the assumption of less strict or missing control of antibiotic usage (Xian et al., 2018; Zhao et al., 2010).

Record on rainfall and soil moisture dynamics continued throughout the rainy season of 2021, and prediction on occurrence of surface runoff was based on changes in soil water potential (see data in Fig. S1). Instantaneous rainfall intensity was recorded based on precipitation of every 15 min during the rainfall process (shown as inverted blue columns in Fig. 2). Two continuous rainfalls were monitored on August 7th (event 1) and 22nd (event 2). They were both rainstorms with a maximum instantaneous rainfall intensity of 44.0 and 74.4 mm/h, respectively. The precipitation and duration were 81.4 mm and 15.5 h for event 1 and 128.8 mm and 18.75 h for event 2, with the corresponding rainfall intensity of 5.25 and 6.87 mm/h, respectively. The two events accounted for 15 % of the total precipitation (1389.2 mm) of the year. Whenever available during the rain, a certain volume of surface runoff samples (500 mL to 1.0 L depending on flow rate) was collected manually for every 15 min. To guarantee sample volume, the sampling interval was adjusted to 0.5 h or 1.0 h as the flow rate decreased until rain ended. Upon collection, samples were immediately transferred to the laboratory for pretreatment processing and subsequent analysis.

2.2. Source of chemicals and reagents, pretreatment and antibiotic analyses

Eight antibiotics including sulfadiazine (SDZ), sulfamethazine (SMZ), florfenicol (FFC), tetracycline (TC), oxytetracycline (OTC), norfloxacin (NOR), enrofloxacin (ENR) and tylosin (TYL) were selected as target contaminants due to their wide usage and frequent presence in the aquatic environment of the study area. The compounds were purchased from Aladdin Chemical Reagent Co. Ltd., China (≥98 %) for field application and from Dr. Ehrenstorfer GmbH (≥99.5 %) for chromatographic analysis and the quenching experiment, respectively. Internal standards (sulfamethazine-d4, norfloxacin-d5, tetracycline-d6, chloramphenicol-d5, and roxithromycin-d7) were obtained from Dr. Ehrenstorfer GmbH (≥99.5 %). A detailed information on the source and preparation for the above and other chemical reagents is shown in the attached Supplementary Information. Samples of surface runoff were 0.45 μm filtered (hydrophilic polypropylene) and extracted using Oasis HLB cartridges (3 mL, 100 mg) (Milford, Massachusetts, USA). Following purification and elution, the antibiotics were analyzed using ultra-performance liquid chromatography-tandem mass spectrometer (UPLC-MS/MS) (Framingham, Massachusetts, USA). Detailed mass spectrometry information, the recoveries of the extraction method and the quality control parameters are given in Fig. S2 and Tables S3–S4.

The concentration of dissolved organic carbon (DOC) was determined for the filtered surface runoff samples using a TOC analyzer (Aurora 1030C, OI Analytical, USA). Colloidal particles (<10 μm) were extracted from the runoff samples by sedimentation method and the colloidal concentration was determined at 400 nm using ultraviolet-visible (UV–vis) spectrophotometer (TU-1810, China). The particle size distribution (PSD) was measured using a laser particle size analyzer (LA950, Horiba JY, Japan).

Fig. 1. Schematic picture of experimental plots with rainfall monitoring and surface runoff sampling facilities (CP, control plot; MFP1/2, parallel manure-fertilized plots).
Notes: 1. Rain gauge; 2. Ceramic suction lysimeter (10 cm depth, blue); 3. Ceramic suction lysimeter (30 cm depth, purple); 4. Surface runoff confluence trough; 5. Self-made surface runoff tipping bucket; 6. Self-made surface runoff collection tank; 7. Data acquisition toolbox (CR1000 Mainboard).

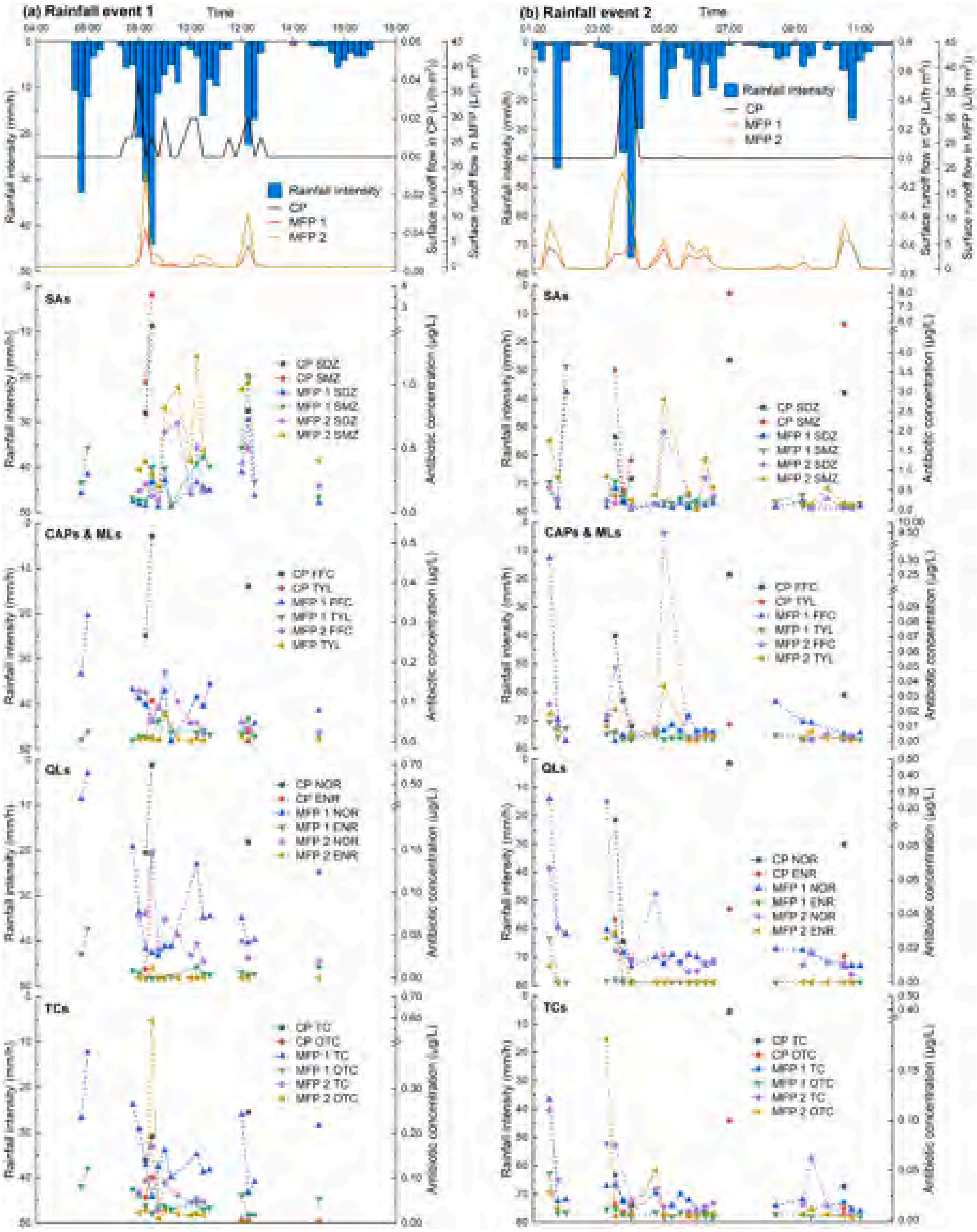

Fig. 2. Dynamics of surface runoff flow rate and antibiotic concentrations in response to rainfall intensity during two consecutive rainfall events (CP: the control plot; MFP1,2: the parallel manure-fertilized plots).

2.3. Spectroscopy and PARAFAC modeling

Simultaneous measurement of UV–visible absorbance and excitation-emission matrix (EEM) fluorescence spectra was made by an Aqualog fluorescence spectrometer (Horiba JY Aqualog, Japan). Water Raman peak and emission calibration validation were used to make sure the CCD detector was stable. UV absorbance was measured from 200 to 600 nm, and fluorescence spectra were obtained across emission wavelengths (E_m) of 240–600 nm at excitation wavelengths from 240 to 500 nm with 5 nm increments and an integration time of 0.5 s. Milli-Q EEM was used as blank to remove the instrument-specific spectral biases. Inner-filter effects (IFE), Raman bands and Rayleigh scatters were corrected by the built-in software (Wang et al., 2017). Parallel factor (PARAFAC) modeling was performed using SOLO software (Eigenvector

Research Inc., USA) (Xian et al., 2018). The spectra were constrained to non-negative values, primary Rayleigh scatter was set to missing values, and Raman bands and secondary Rayleigh scatter were replaced by interpolated values (Stedmon and Bro, 2008). Residuals, core consistencies and split-half analysis were used to validate the model results (Bro, 1997; Murphy et al., 2013). According to the shape and location of spectra peaks, DOM components were identified after referring to previous studies. Based on model results, the maximum fluorescence intensity (F_{max}) was obtained by multiplying the M1 loading score by the maxima of emission and excitation loadings (M2 and M3). The F_{max}/DOC was then used to represent the content for each identified component, which is a normalized value by dividing F_{max} by the DOC concentration of the sample (Zhang et al., 2019).

2.4. Fluorescence quenching experiment and 2D-COS analysis

The manure DOM was obtained from water extraction and 0.45 μm filtration of fresh chicken manure collected in the field. The quenching test was performed in triplicate by adding 10 mL of each DOM solution (100 mg C/L) to 50 mL antibiotic solutions of a series of concentrations (1.0, 2.0, 5.0, 10.0, 15.0, 20.0 and 25.0 mg/L) with a 10 mmol/L $CaCl_2$ and 0.1 g/L NaN_3 background. The reaction system was incubated for 8 h in an end-over-end rotating mixer (T = 298, pH = 9, n = 180 rpm), followed by EEM fluorescence measurement. Antibiotic compound was reacted separately to avoid interference. Quenching EEMs were calculated by subtracting EEMs for the antibiotic-DOM system from that of corresponding DOM alone. Except for quinolones and tetracyclines, contribution of antibiotics themselves to the total fluorescence was found to be insignificant relative to manure DOM across the EEM range employed, such that quenching spectra represent the diminished DOM fluorescence in the presence of antibiotics.

The antibiotic-DOM interaction parameters were calculated from the obtained quenching spectra data by the Stern-Volmer equation (Eq. (1)) and site binding equation (Eq. (2)) (Zhang et al., 2022b; Ferrie et al., 2017).

$$\frac{F_0}{F} = 1 + K_q\tau_0[Q] = 1 + K_{sv}[Q] \quad (1)$$

$$log\frac{F_0 - F}{F} = logK_b + nlog[Q] \quad (2)$$

where F_0 and F are the fluorescence intensity of chicken manure DOM prior to and after incorporation of antibiotics as quencher (the emission spectra at a fixed excitation wavelength of 275 nm were used); K_q is the bimolecular quenching constant (L/(mol·s)); K_{sv} is the Stern-Volmer quenching constant (L/mol); τ_0 is the average fluorescence lifetime of macromolecules without quenchers, which is generally 10^{-8} s; $[Q]$ is the quencher concentration; K_b is the binding constant (L/mol); n is the binding site number.

Two-dimensional correlation spectroscopy (2D-COS) analysis on the quenching EEMs was also performed to help us obtain authentic details about the fluorophore changes induced by the antibiotics binding (Noda, 2016). Open-source software 2D-shige (Kwansei Gakuin University, Japan) (Maqbool and Hur, 2016) and Origin 2021 software (Originlab, USA) were used to draw the synchronous and asynchronous spectroscopy for each target antibiotic.

2.5. Statistics

Spearman correlation analysis was performed using R 3.6.2 (http://cran.r-project.org/) for correlating the antibiotics with F_{max}/DOC, colloidal concentration, particle size distribution (PSD) <10 μm data and DOC values. Significant differences were considered at a $p < 0.05$. The redundancy analysis (RDA) was performed using Canoco 5 (Microcomputer Power, USA).

3. Results and discussion

3.1. Surface runoff observation during rainfalls

Generation of surface runoff was observed to have a clear response to the instantaneous rainfall intensity, and it was tremendously increased due to chicken activities that had changed plot surface. During the rainfall event 1 (Fig. 2a), due to long period of soil dryness prior to the rain, no surface runoff was generated as the rainfall intensity reached the first peak at 5:45 a.m. Later, surface runoff was observed at around 7:00 a.m., with the following ups and downs occurred responding to rainfall intensity. It was also observed that, the flow rate for surface runoff from MFP1 (7.55 L/(h·m^2)) and MFP2 (19.17 L/(h·m^2)) plots was much higher than that of the CP control (0.04 L/(h·m^2)) ($p < 0.05$). During the rainfall event 2 (Fig. 2b), surface runoff was observed as the rain started at 1:00 a.m. The runoff production was fast because of the relatively high soil moisture content due to the previous rain. As the rainfall reached its peak intensity at 4:00 a.m., peak flow of surface runoff occurred accordingly, with the rates for the MFP plots (4.84 and 19.36 L/(h·m^2)) still significantly higher than that of CP (0.73 L/(h·m^2)). The soil was then saturated and the surface runoff in the MFP plots reached a second flow peak (5.89 and 8.80 L/(h·m^2)) ca. 7 h later at 11:00 a.m. It should be noted that the difference in flow rate between two parallel plots was mainly due to soil heterogeneity and differences in soil surface and chicken activities under natural conditions.

Due to free-range chicken raising, there was almost no weed coverage on soil surface and the soil was trampled hardly by chickens so that it became bare and compact in the MFP plots. Without loose soil texture and weeds, therefore, the production of surface runoff was considerably increased. The results from our measurement of soil saturated hydraulic conductivity (K_S) have provided evidence for the changes. As compared to 217.82 cm/d for the CP treatment, much lower K_S values were obtained for the MFP parallel plots (73.34 and 65.68 cm/d, respectively, Table S2 of the SI), indicating reduced soil permeability and subsequent increased runoff generation upon saturation.

3.2. Antibiotic concentrations in the surface runoff

All target antibiotics were found in the collected surface runoff samples, with a detection rate >95 % and the concentrations mostly at the μg/L level. As shown in Fig. 3, concentrations for the same category of antibiotics, such as SDZ and SMZ or TC and OTC, were similar and in the same order of magnitude. Among them, sulfonamides (SDZ and SMZ) showed the highest concentrations of 10^{-2}–10^{0} μg/L, while tetracyclines (TC and OTC) and fluoroquinolones (NOR and ENR) were the lowest of 10^{-6}–10^{-2} μg/L, respectively. Besides high levels of sulfonamides, the concentration of a chloramphenicol antibiotic (FFC) was also high, while a macrolide antibiotic (TYL) was at a similar level with fluoroquinolones.

These observations are similar with previous reports from other regions of the country, such as the hilly peri-urban area of Yangtze River Delta in eastern China (Zhao et al., 2020), and the vegetable fields of Pearl River Delta in southern China (Gu et al., 2021). The mean concentration for different categories of antibiotics followed the order of SAs > FFC > TYL > TCs > QLs, which is mostly consistent with the adsorption characteristics of antibiotics in the soil. According to present studies (Li et al., 2018; Li et al., 2012), QLs and TCs antibiotics have strong adsorption so that they usually remain largely in the soil, while on the other hand, antibiotics of SAs and FFC are easily lost to surface runoff and leachate at high concentrations due to weak affinity to soil.

A significant difference between MFP and CP treatments ($p < 0.05$) is worth noting. Relatively lower concentrations were observed for the MFP plots, and this is mainly due to the dilution effect by a much higher flow rate and runoff yield as compared to the control (data not shown).

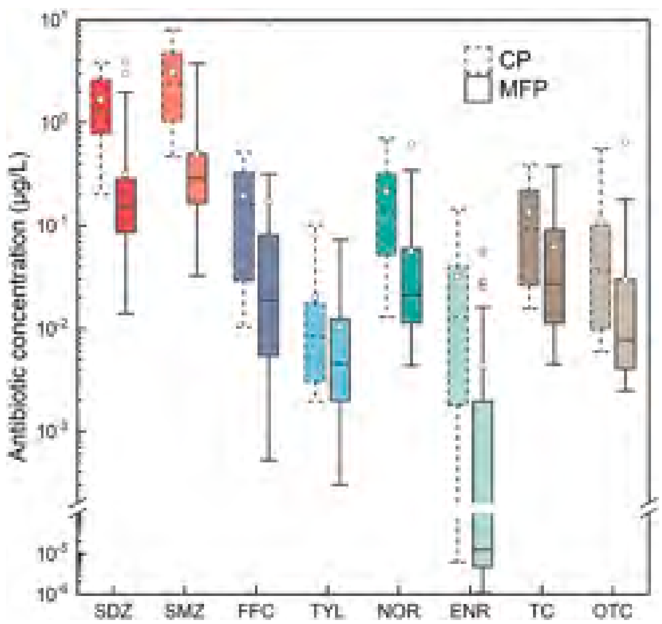

Fig. 3. Concentrations of various antibiotics in the surface runoff during rainfalls (MFP and CP stand for the chicken-raising treatment and the control, respectively; MFP contains data of MFP1 and MFP2).

3.3. Dynamics of antibiotics migration responding to rainfalls

Due to difference in runoff production, more samples (41 and 32) were obtained from the MFP plots and only 8 samples were collected from the CP plot. As depicted in Fig. 2, concentrations for all antibiotics had an obvious response to the instantaneous rainfall intensity, with the concentration peaks occurred with the rainfall intensity peaks with almost no time difference. Under rainfalls, antibiotics in the soil desorbed continuously into the soil pore water, so that the concentration increased rapidly in the runoff water once the soil reached saturation state. The concentration peak for antibiotics mostly occurred with the initial rainfall intensity peak, and the concentration decreased afterwards due to dilution of rainwater, and rose up again at the following rainfall peak.

An obvious fluctuation of the concentration was observed for sulfonamides, indicating they are a sensitive type of antibiotics towards rainfalls. Once they migrate from farmland to the river, they continue to transport along the waterway so that it would be detected with high frequency, which coincides with the reported prevalence of these compounds in the affected watershed and even wider environment (Liu et al., 2013). FFC was also sensitive, and on the other hand, QLs and TCs appeared to be more likely to remain in the soil due to strong affinity to soil particles. Even when flushed away via surface runoff or leached out, they are easy to deposit on riverbed with particulate sediment, rather than existing in the water along the river channel (Gu et al., 2021; He et al., 2019).

Although antibiotic concentrations for the MFP plots were relatively lower than the control (Fig. 3), it can be concluded that migration of antibiotics would be tremendously increased in consideration of the pretty high runoff flow under chicken-raising treatment. By calculation with the runoff yield (data not shown), for instance, the total loss of SDZ and SMZ in rainfall event 1 was 12.30 and 16.53 μg for the CP treatment, while the average loss from two parallel MFP plots was up to 134.03 and 500.36 μg, respectively. The result is consistent with a previous report on antibiotics transport in an aqua-agricultural catchment (Dong et al., 2021). It was observed that continuous rainfalls resulted in pollutants migration at low concentrations but a significant total loss due to high runoff yield. From this perspective, consideration of soil structure and hydraulic feature is of significant importance in assessing runoff production and pollutant migration on a field or larger scale. The present study has thus provided a clue of land use impact for the elevated antibiotics transport due to soil changes under chickens raising treatment.

3.4. Spectroscopy of DOM components and their dynamics during rainfalls

According to EEM fluorescence measurement coupled with PARAFAC analysis, DOM in the surface runoff consisted of three major components, with EEM peaks located at the excitation/emission wavelengths (E_x/E_m) of 260(400)/480 nm (Component 1, C1), 270(380)/430 (Component 2, C2) and 270/370 nm (Component 3, C3), respectively (Fig. 4 and Fig. S4 of the SI). These components have been previously identified in the literature and defined as humic-like (C1), fulvic-like (C2) and protein-like (C3) components. Specifically, C1 belongs to long-wave humus, which is ubiquitous and of the highest content in forest environment (Cory and McKnight, 2005); C2 represents short-wave fulvic acid that derived from terrestrial plants or soil organic matter, which has a smaller molecular weight and higher fluorescence efficiency (Xian et al., 2018); C3 is mainly composed of tryptophan, which is produced from endogenous or microbial processes representing intact protein or less degraded peptides (Cory and McKnight, 2005).

As shown in Fig. 4, the content for DOM components in the surface runoff was presented using the normalized maximum fluorescence intensity based on PARAFAC modeling results (Xian et al., 2018). It has indicated that all the three components responded obviously to the rainfall intensity. When the rain started, their contents dropped rapidly, and then increased gradually as the rainfall intensity decreased. The peaks for the DOM components were observed to lag for a certain period of time from 15 to 30 min following the corresponding rainfall intensity peaks.

For the MFP plots, the content for the protein-like component (C3) was always higher than that of the other two components (C1 and C2) during the rainfalls ($p < 0.05$). The F_{max}/DOC values for C3 in the MFP plots were also significantly higher than that of the CP ($p < 0.05$). The prominent presence of C3 in the collected runoff samples was attributed to the continuous input of manure discharged on soil surface by chickens. The protein-like component was produced from the manure substrate through biodegradation and leaching. According to literature, the chicken manure DOM mainly consists of tryptophan, which accounts for majority of the C3 fluorescence intensity (Zhang et al., 2019).

3.5. Potential use of spectroscopic indices for tracing antibiotics migration during rainfalls

As the optical properties of DOM in relation to antibiotics have been explored in the past years, the present study established correlations of DOM fluorescence indices with antibiotics via field-scale surface runoff migration. According to literature, DOM components have been found to link with occurrence of antibiotics in natural aquatic environment including rivers (Zhang et al., 2015), catchments (Dong et al., 2021), city-river-reservoirs (Zhang et al., 2019) etc. Such correlations were also found in engineering processes such as the advanced oxidation treatment of wastewater (Anjali and Shanthakumar, 2019). These studies have demonstrated great potential of using fluorescence technique as an approach for water quality monitoring, probing not only conventional pollutants but trace-level ones of emerging concern. Due to high efficiency and sensitivity of the spectrum, the approach is assumed to be particularly suitable for online monitoring of dynamic processes. As shown herein, robust positive correlations between the contents of C1, C2 and C3 components as represented by F_{max} values and the antibiotic concentrations were observed during the rainfalls ($p < 0.05$). Consistent results were obtained from the Spearman correlation analysis (Fig. 5) and the redundancy analysis (see data in Fig. S3 of the SI). Among the three PARAFAC-identified DOM components, C3 was found to be the

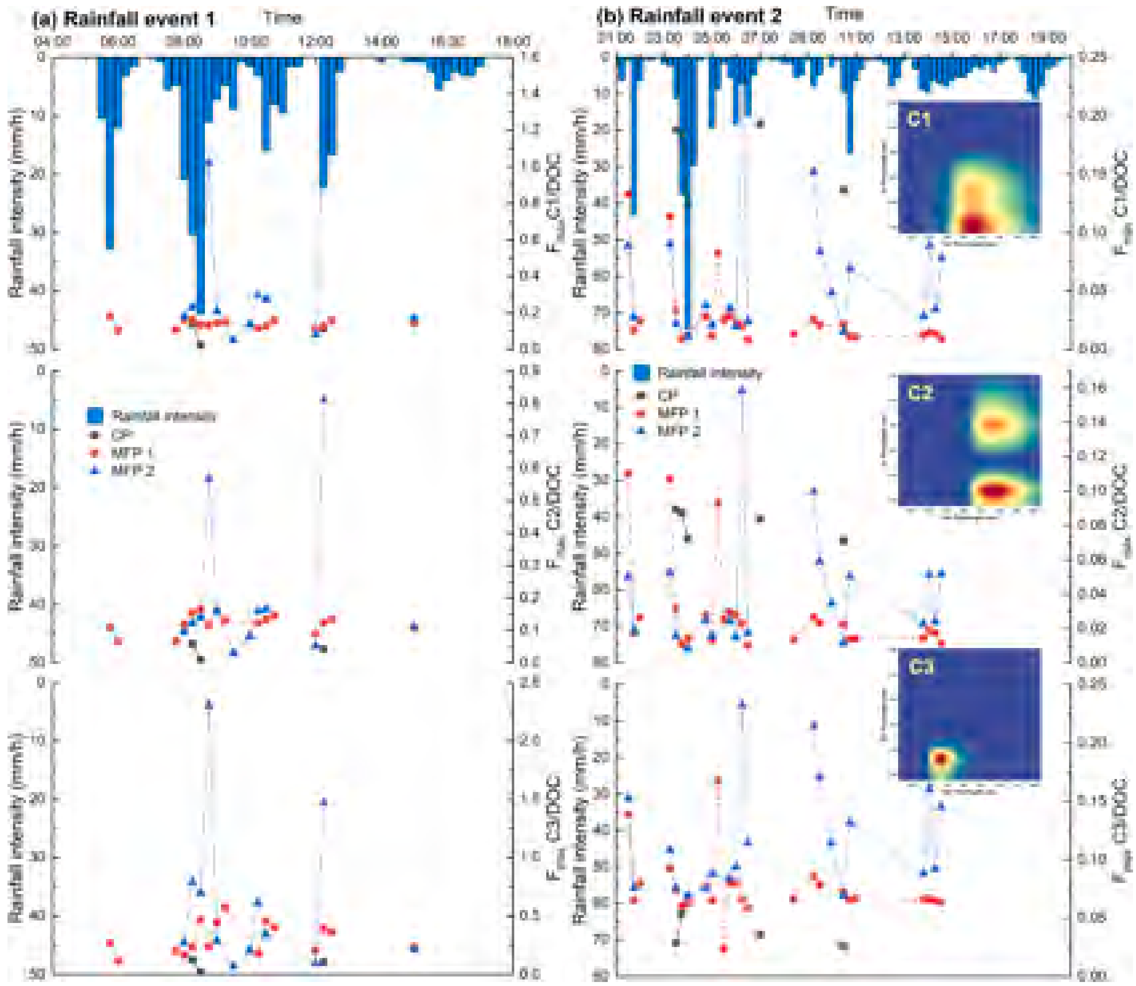

Fig. 4. Dynamics of the normalized maximum fluorescence intensity (F_{max}/DOC) of PARAFAC-identified DOM components in surface runoff corresponding to the observed rainfalls. (The embedded graphs are fingerprint EEMs for the deconvolved components C1, C2 and C3).

most significantly correlated with antibiotics. RDA analysis also showed that F_{max} C3/DOC accounted for 72.6 % of the contribution rate ($p < 0.05$). Besides, the degree of correlation varied among the different types of antibiotics. To be specific, stronger correlations were found for fluoroquinolones and tetracyclines as compared to that for sulfonamides, FFC and TYL. The presence of these correlations is an empirical evidence of co-migration and interactions of DOM and antibiotics via the runoff process. Soil column studies have observed facilitated transport of antibiotics in the presence of manure-derived colloids or DOM (Zhang et al., 2019). The underlying mechanism of the interactions and an interpretation of the differences among the DOM components and among the antibiotics were explored in the final section of this article.

Additionally, DOC concentrations were in the ranges of 5.79 to 106.70 mg/L for the CP plot and 0.44 to 74.28 mg/L for the MFP plots, respectively, with no significant difference between the two treatments ($p > 0.05$). There was no significant correlation between DOC and antibiotic concentrations ($p > 0.05$). Consistently, the RDA analysis showed that the contribution of DOC to the antibiotic concentrations was 1.1 %. Correlations were only found for DOC with F_{max} values, as DOC concentration is an accepted measure of chromophoric DOM content in natural waters (Singh et al., 2010).

Interestingly, concentrations of colloids and particles of <10 μm had both shown negative correlations with some antibiotics. It is known that antibiotics can migrate either in dissolved state or in association with colloids and suspended particles. Previous study has demonstrated that colloids from 1 nm to 10 μm may act as contaminant carriers via runoff migration (Kan and Tomson, 1990). For antibiotics with high adsorption potentials, mobile particles in bigger size can lead to an enhanced transport in soils (Luo et al., 2019). In this study, as antibiotics were analyzed following filtration of the sample, only the dissolved part of the compounds was quantified. Statistically nonsignificant and significantly negative correlations were observed. For NOR, ENR, TC, OTC and TYL, the correlation coefficient was −0.32, −0.27, −0.37, −0.16 and −0.29, respectively ($p < 0.05$). It seems that the stronger their association with colloids and particles, the more negative the correlation for the antibiotic in dissolved form. Here we can assume that the residual part of antibiotics left on the filter membrane may be positively correlated with the colloids and particles. On the other hand, no significant correlations were found for SDZ, SMZ and FFC ($p > 0.05$), which is also reasonable given the weak binding abilities of these compounds to colloids and particles.

3.6. Manure DOM-antibiotics correlations based on their binding interactions

Until now, fluorescence quenching tests on examining antibiotic interactions have been conducted mostly using standard or model substances rather than freshly-extracted manure DOM (Huang et al., 2022; Zhang et al., 2022b; Zhao et al., 2019). The manure DOM consisted of protein-like substance, particularly the tryptophan (Ex/Em 275 nm/305–315 nm), and humic-like moieties (Ex/Em 275 nm/545–550 nm) (Fig. S4 of the SI). Due to quenching, the manure DOM fluorescence was decreased gradually in response to the addition of antibiotics with increasing concentrations (Fig. S5 of the SI). At the highest quencher

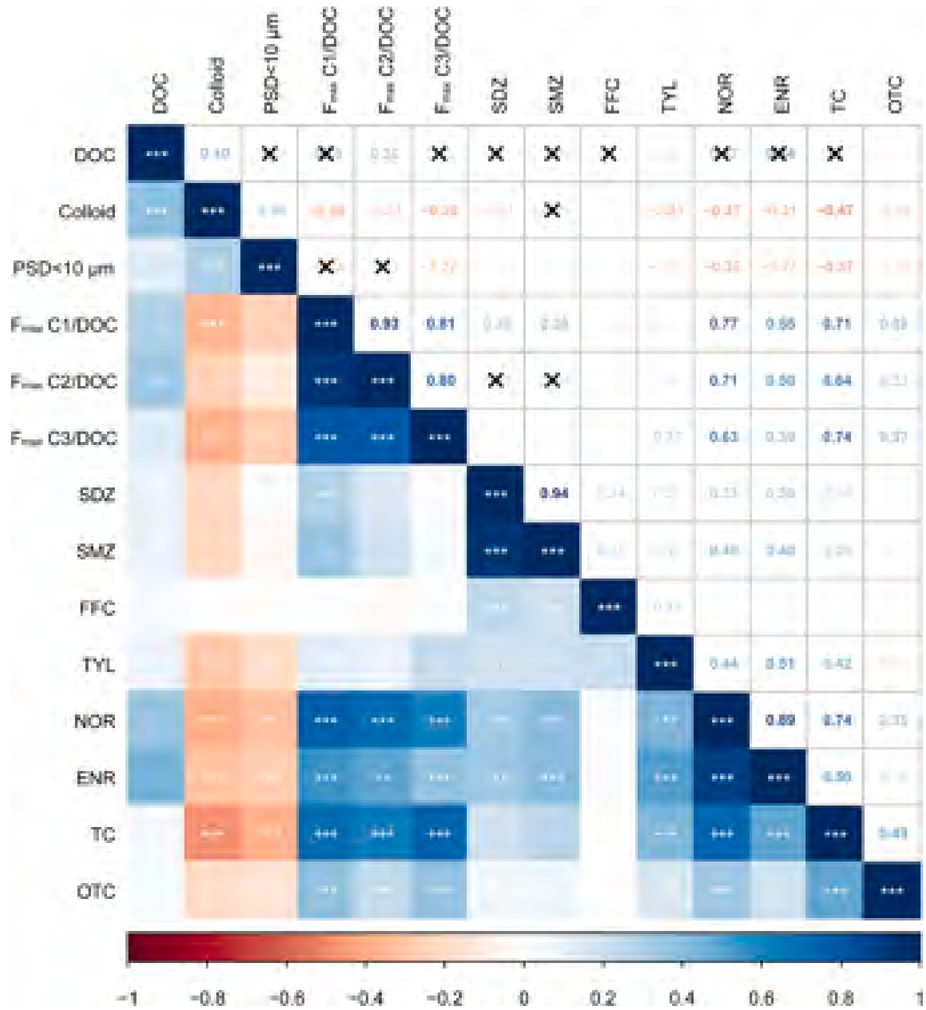

Fig. 5. Spearman correlations of concentrations of DOC, colloids, particles in size of <10 μm (referred as "PSD < 10 μm") and the F_{max} values with antibiotic concentrations for the surface runoff collected during rainfalls (DOC: dissolved organic carbon; F_{max} C1, C2, C3: maximum fluorescence intensity of PARAFAC-identified components C1, C2 and C3).

dose, the peak intensity was diminished by 93.45 % and 92.37 % for NOR and ENR, 88.94 % and 88.40 % for TC and OTC, 78.19 % for TYL, 87.40 % and 88.72 % for SDZ and SMZ, and 47.38 % for FFC, respectively. Also, a blue-shift of ca. 10 nm for the tryptophan peak was observed as the fluorophore being placed in a more hydrophobic environment after antibiotics binding (Xu et al., 2013).

To better identify the fluorophore changes induced by antibiotics, 2D-COS spectra were obtained from the quenching EEMs where intensities and signs of related peaks can be interpreted by the principles proposed by Noda and Ozaki (Noda and Ozaki, 2004). In the synchronous map, auto-peaks with positive signs suggest perturbed spectral intensities, whereas cross-peaks represent the direction of the intensity change at the corresponding coordinates. For all antibiotics, there are two positive auto-peaks at 315 nm and 550 nm on the diagonal, representing the quenched tryptophan and humic-like component of the manure DOM pool, respectively (Fig. 6). Positive sign of the corresponding cross-peaks indicated that the intensity for both components decreased with the increase of antibiotic concentration. The peak intensity at 315 nm was found to be greater, suggesting stronger bindings to tryptophan than the humic-like component. The peak at 400–450 nm for NOR and ENR accounts for the contribution of antibiotics themselves to the total fluorescence and thus was irrelevant relative to the manure DOM zone. Similarly, the auto-peak at 500–600 nm for TC and the observed negative cross-peak also reflects the increased intensity of the antibiotic itself. In the asynchronous map, where cross-peaks present exclusively, the signs reveal the sequential order of the spectral variations. Accordingly, the opposite signs of the coordinate (550, 315) in the synchronous and asynchronous maps indicate that change of the spectral intensity at 315 nm occurs prior to 550 nm. Thus, it suggests that antibiotics interact preferentially with the tryptophan moiety rather than humic-like species of the manure DOM pool.

The quenching data were further fitted using the Stern-Volmer equation to a single linearity for each antibiotic (see the fitting lines in Fig. S6 of the SI) (Cheng et al., 2020). To explore the difference in the binding ability among varying antibiotics, the quenching constant (K_{sv}), the binding constant (K_b) and site number (n) were calculated accordingly (Zhu et al., 2019). As shown in Table 1, the K_{sv} and K_b constants were both in the order of quinolones (NOR, ENR) > TYL > tetracyclines (TC, OTC) > sulfonamides (SDZ, SMZ) > FFC, indicating that the complexation potential of quinolones and tetracyclines could be greater than other antibiotics. Reported K_b values were in the range of 2.0 to 8.0 $\times 10^4$ L/mol for antibiotics-humic acid system and 2.11 to 58.4 $\times 10^4$ L/mol for antibiotics-ovalbumin system (Zhang et al., 2022b). In comparison, the K_b was up to 13.17 $\times 10^6$ L/mol in this study, suggesting quite strong bindings between antibiotics and chicken manure DOM. Due to DOM's complex molecular structure with active functional groups, antibiotics are reported to bind to DOM mostly through covalent complexation reactions including hydrogen bond, Van der Waals force, electrostatic, hydrophobic effect and π-π stacking (Zhao et al., 2019). Here, the higher binding affinity is consistent with the higher

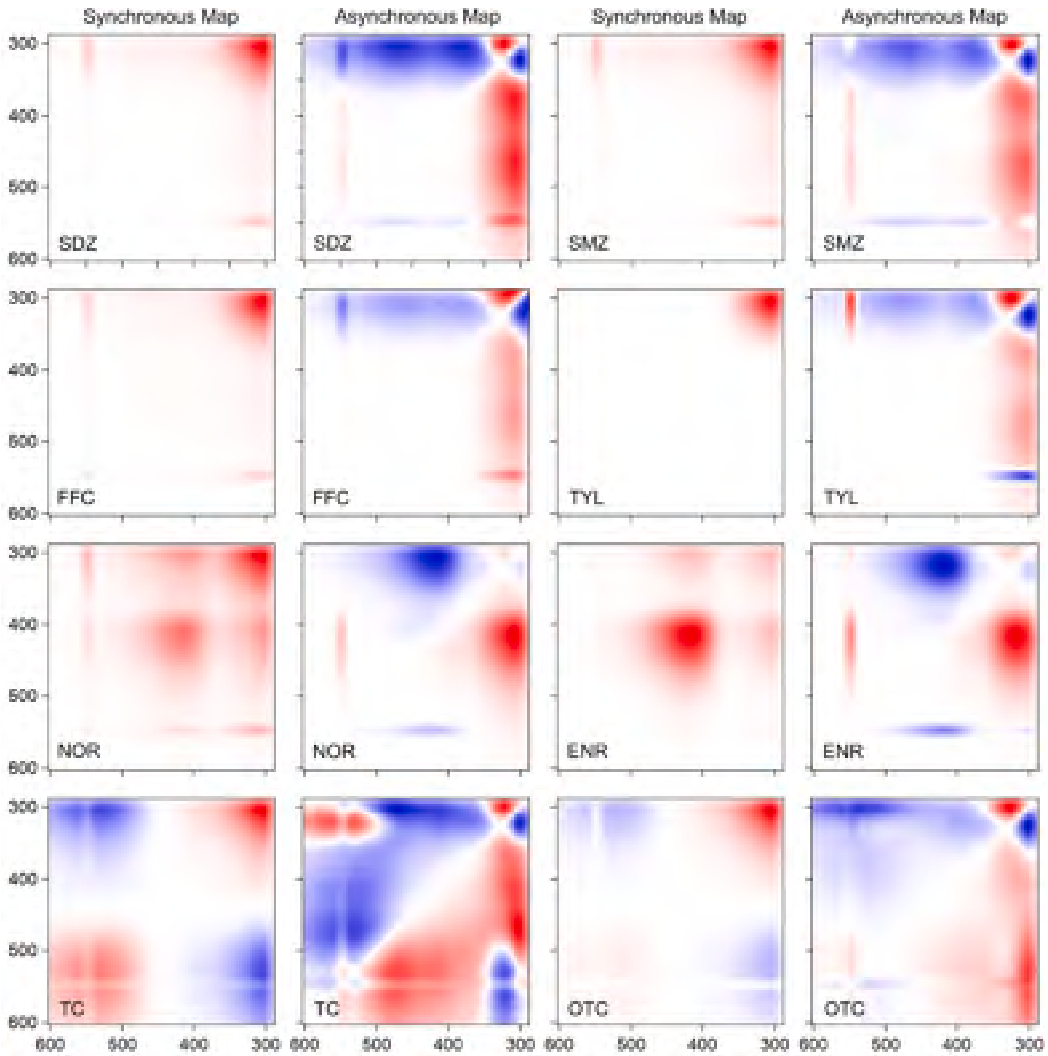

Fig. 6. Synchronous and asynchronous 2D-COS maps obtained from the fluorescence emission spectra from 280 to 600 nm at an excitation wavelength of 275 nm after quenching chicken manure-derived DOM with eight target antibiotics of varying concentrations.

Table 1
Fitting parameters of the Stern-Volmer equation and site binding equation for antibiotics bound to chicken manure-derived DOM based on fluorescence quenching test data.

Antibiotics	T (K)	K_{sv} (10^5 L/mol)	K_b (10^6 L/mol)	n	R^2
SDZ	298	0.7037	2.0188	1.35	0.9905
SMZ	298	0.7999	2.2591	1.43	0.9969
FFC	298	0.2260	0.0121	0.94	0.9914
TYL	298	1.5088	6.5073	1.34	0.9897
NOR	298	2.0344	13.1743	1.38	0.9982
ENR	298	1.5268	8.7700	1.42	0.9920
TC	298	1.4099	6.4699	1.37	0.9953
OTC	298	1.3807	6.1024	1.37	0.9957

significance level of antibiotic-DOM correlations. For QLs and TCs, thus, their migration via surface runoff is more likely to be facilitated by mature DOM. On the other hand, SAs and FFC are readily highly mobile so that less relatively influenced by manure presence.

4. Environmental significance

Orchard with free-range chickens is a popular ecological farming mode in rural China. However, contamination of chicken manure-sourced antibiotics from orchard soils to ambient waters is a major concern. The present study has demonstrated that land use, soil structure and rainfall conditions jointly affect the concentration variability of antibiotics in surface runoff process. Under the circumstance of rainstorms, antibiotics particularly those with strong adsorption capacities in soil can be flushed away in the beginning of runoff production. Due to chicken activities, the runoff flow will be considerably increased as compared to orchard without chickens, which would result in a high total migration of antibiotics. Therefore, the practice of raising chickens in orchard is posing a potentially high risk of contamination to the surrounding environment.

The results of this study also highlight a necessity of observing soil structure and hydraulic properties in assessing the runoff transport of contaminants. In chicken-raising orchard, reduced porosity and saturated hydraulic conductivity were observed for the surface soil, and this finding provided evidence for the elevated runoff flow and the subsequent increased antibiotics output. Undoubtedly, more research should be warranted to find key factors and the underlying mechanisms driving the antibiotics migration in consideration of the very diverse characteristics of different soils. Besides, erosion sediment should be taken into account as it also contributes to contaminant migration in runoff. More observation data are also needed in the future for fully understanding the contaminant hydrology under varying rainfall conditions and at different field scales.

5. Conclusions

This study observed field-scale migration of antibiotics via surface runoff in rainfall events. Rainstorms resulted in continuous antibiotics output from the start of runoff production. During rainfalls, antibiotic concentrations fluctuated in responding to instantaneous rainfall intensity. Highly mobile sulfonamides and florfenicol migrated at much higher concentrations than those with high affinities to soil. Under chicken-raising treatment, antibiotics migration was tremendously enhanced with the increased runoff production as the soil surface became more bare and compact due to chicken activities. Furthermore, antibiotic dynamics were found to correlate significantly with variations of DOM contents. Presence of such correlations was based on antibiotics-DOM interactions, with the significance level for various antibiotics consistent with their respective binding affinity. A preferential binding with the manure-derived tryptophan moiety was observed for all antibiotics. By establishing these correlations, this study has provided rainfall event-based data to demonstrate a feasibility of using fluorescence indices as an alternative to trace dynamic migration of antibiotics.

CRediT authorship contribution statement

Xin-Yu Liu and **Xiao-yun Gu** contributed equally to the field work, sampling and analysis, the collection and processing of experimental data, and the drafting of this manuscript. They should be regarded as co-first authors.

Lanre Anthony Gbadegesin participated in the field work, investigation and interpretation of experimental data.

Chen Liu was in charge of supervising all experimental and interpretative activities, funding acquisition, editing and completing the final version of the manuscript.

Yang He and **Jian-Qiang Zhang** participated in the drafting and editing of the manuscript.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Chen Liu reports financial support was provided by National Natural Science Foundation of China.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2023.168527.

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