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Occurrence of Antibiotics in Water in Xiaodian Sewage Irrigation Area, Northern China

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Abstract. The Xiaodian sewage irrigation area in northern China has a long history of sewage irrigation. The surface water and groundwater samples were collected and analyzed in this region. All the 25 kinds of antibiotics have been detected in the surface water in this study area. The order of average detection frequency is Macrolides (MLs, 98.2%) > Fluoroquinolones (FQs, 91.3%) > Tetracyclines (TCs, 87.5%) > Sulfonamides (SMs, 75.0%). The sample with the highest concentration of antibiotics (730.19 ng/L) is located at Taiyu Drainage Canal while that with the lowest concentration (245.93 ng/L) at Xiaohe River. The type and concentration of antibiotics in SW-3 and SW-4 were almost the same, indicating the measures to prevent canal banks from seepage were able to retard their transport into the soil and groundwater system via lateral recharge. Along the Beizhang Drainage Canal, the sewage from the swine farm, the cow farm, the irrigation field and domestic usage were all discharged into the canal, so the concentration kept increasing. Along the down gradient direction of Taiyu Drainage Canal, the concentration decreased. Transport of the contaminants via lateral recharge due to lack of seepage prevention measures, therefore, poses a potential threat to the soil-groundwater system. 15 of 25 kinds of antibiotics were detected in the groundwater. The detection frequency was lower than other study areas in China. The concentrations ranged from 2.75 ng/L to 114.38 ng/L with the average concentration of 27.60 ng/L.

1. Introduction
Because of lack of water resources, sewage irrigation has had a long history in Taiyuan city[1] and this sewage irrigation area has become one of the major sewage irrigation areas in the north of China. By 1995, the city's total irrigation area was 834,000 mu while effective irrigation area was 812,000 mu[2], the annual irrigation requirement was 178.2 million m$^3$. Under the situation of water shortage, it is difficult to ensure that all of them irrigated by clean water. At present, More than 200 million m$^3$ of industrial sewage and domestic sewage from the urban area is mostly discharged into Fenhe River. With the increase of sewage irrigation frequency and quantity of the sewage irrigation, environment quality of the surface water and groundwater were affected in some regions. The environmental conditions in Taiyuan City sewage irrigation area were studied by some researchers. However, the report for organic pollution of sewage irrigation area was much less. Zhang et al. studied the influence of long-term sewage irrigation to the distribution of organochlorine pesticides in water and soil[3]. Li et al. reported the distribution and sources of polycyclic aromatic hydrocarbons in the topsoil of the
sewage irrigation area[1]. Liao researched the adsorption behavior of nonylphenol in sewage irrigation area[4]. However, there has been no systematic study on the environmental geochemical behavior of antibiotics in sewage irrigation area[5]. The objectives of this study are systematically study about the environmental geochemistry behavior of antibiotics in the surface water and groundwater, analyse the distribution, source and migration of these organic contaminate in the environment.

2. Materials and methods

2.1. Site description
Because of lack of water resources, sewage irrigation has had a history of nearly 40 years in Taiyuan city, and this sewage irrigation area has became one of the major sewage irrigation areas in the north of China. By 1995, the city's total irrigation area was 834,000 mu while effective irrigation area was 812,000 mu, the annual irrigation requirement was 178.2 million m³. Under the situation of water shortage, it is difficult to ensure that all of them irrigated by clean water. At the same time, low cost is another major reason promoting the development of sewage irrigation. At present, More than 200 million m³ of industrial sewage and domestic sewage from the urban area is mostly discharged into Fenhe River. According to statistics, in the "Eighth Five Year Planning" period (1991-1995), Taiyuan sewage irrigation area was 394,500 mu, accounting for 47.3% of the total irrigation area; the annual irrigation water capacity was 95.85 million m³, accounting for 53.7% of total agricultural irrigation water.

2.2. Sampling
A summary of 14 surface water samples and 9 groundwater samples were collected in the study area. Fig. 1 shows locations of surface water samples and groundwater samples. Surface waters included Fenhe River water, Xiaohe River water, water from East Main Canal and water from drainage canals. Groundwaters were all collected from wells with depth between 15 m and 35 m after 10 minutes’ pumping to get fresh samples, and then stored in 4 L amber glass bottles at 4°C and treated as soon as possible.
Figure. 1 Location of water samples collected from Xiaodian sewage irrigation area

2.3. Analysis
The target antibiotics can be divided into 4 categories: (1) sulfonamides (SMs): Sulfapyridine (SPD), Sulfathiazole (STZ), Sulfamethoxazole (SMX), Sulfamerazine (SMR), Sulfamethazine (SMZ), Sulfamethoxypyridazine (STP), Sulfameter (SFM), Sulfadiazine (SDZ); (2) fluoroquinolones (FQs): Ofloxacin (OFL), Lomefloxacin (LOM), Ciprofloxacin (CIP), Enrofloxacin (ENR), Norfloxacin (NOR), Sparfloxacin (SPA), Gatifloxacin (GAT), Fleroxacin (FLE), Enoxacin (ENO); (3) macrolides (MLs): Roxithromycin (RTM), Clarithromycin (CTM), Azithromycin (AZM), Erythromycin (ERY); (4) tetracyclines (TCs): Tetracycline (TC), Oxytetracycline hydrochloride (OTC), Chlorotetracycline hydrochloride (CTC), Doxycycline hydrochloride (DOC).

The samples were extracted using the methods of preview studies[6]-[7]. The antibiotics were analyzed by high-performance liquid chromatography - electrospray ionization tandem mass spectrometry (HPLC-ESI-MS/MS), using the MRM mode. Simetone was used as the internal standard compound. The concentrations were calculated based on the internal calibration curves.

3. Results and discussion
3.1. Antibiotics in surface water
All the 25 kinds of antibiotics have been detected in the surface water. Among them, RTM, CTM, ERY, CTC, OFL, GAT, FLE, OFL, ENR, NOR, SMZ, SMX, SDZ and SPD were 100% detected. AZM, CIP and ENO were 92.9% detected. OTC and DOC were 85.7% detected. TC and SPA were 78.5% detected. STP and STZ were 64.3% detected. SFM were 50.0% detected. Only 21.4% of surface water contains SMR. Order of average detection frequency is as follows: MLs (98.2%) > FQs (91.3%) > TCs (87.5%) > SMs (75.0%). Luo reported the order of the first-order attenuation rate
coefficients (K values) for these 4 classes antibiotics is TCs (K ranged from 0.39 to 1.22 h\(^{-1}\)) > MLs (0.09 to 0.48 h\(^{-1}\)) > FQs (0.08 to 0.45 h\(^{-1}\)) > SMs (0.01 to 0.44 h\(^{-1}\))[8]. Comparing with the detected ratio and attenuation rate coefficients, it could be indicated that there are lots of TCs enter into the surface water.

The highest concentration of antibiotics (730.19 ng/L) occurs at SW-6, this is because SW-6 is located at the intersection of Beizhang Drainage Canal and Taiyu Drainage Canal, the antibiotics of both the canals integrate to this site. The site SW-11 has the lowest concentration (245.93 ng/L). FQs is the main contaminant in the East Main Canal. TCs, FQs and MLs is the main contaminant in the beginning, middle and end of the Beizhang Drainage Canal, respectively. MLs is the main contaminant in the Taiyu Drainage Canal except for the beginning site SW-8, which indicates the concentration of antibiotics in Taiyu Drainage Canal has been strongly affected by the sewage of Beizhang Drainage Canal after they intersected. FQs and MLs is respectively the main contaminant in Xiaohe River and Fenhe River. Summarily, the concentration of antibiotics in surface water shows FQs and MLs are frequently used at the Xiaodian irrigation area, which corresponds to the order of the detected ratio.

Fig. 2 shows the type and concentration of antibiotics in SW-3 and SW-4 were almost the same, indicating that measures to prevent canal banks from seepage were able to retard their transport into the soil and groundwater system via lateral recharge, this is probably the reason why there is a slight increased along the direction of East Main Canal. The site SW-18 has a high concentration of antibiotics, this is because of this site close to the sewage treatment plant. The irrigation water flow the irrigation field from the East Main Canal to Beizhang Drainage Canal, the water quantity has been increased in the Beizhang Drainage Canal, so the concentration was decreased from SW-18 to SW-14. Along the Beizhang Drainage Canal, the sewage which came from the swine farm, the cow farm, the irrigation field and domestic usage were all discharged to the canal, so the concentration kept increasing. Compare with E zone and B zone, we could deduce that the compound NOR is more likely to be adsorbed in the soil or groundwater in the irrigation process. After the intersection of Beizhang Drainage Canal and Taiyu Drainage Canal, the concentration reached the peak at site SW-6. Along the down gradient of Taiyu Drainage Canal, the concentration decreased, transport of contaminants via lateral recharge due to lack of the seepage prevention measures therefore pose a potential threat to the soil-groundwater system.
Figure. 2 The distribution of antibiotics along with the rivers and canals. E: East Main Canal; B: Beizhang Drainage Canal; T: Taiyu Drainage Canal; X: Xiaohe River; F: Fenhe River. The direction of water flow in the rivers and canals are from left to right. Yellow: MLs; Magenta: TCs; Cyan: FQs; Blue: SMs.

3.2. Antibiotics in the groundwater

As Fig. 3 shows, 15 of 25 kinds of antibiotics were detected in the groundwater. The detection frequency was lower than other study areas in China[7]. The concentrations ranged from 2.75 ng/L to 114.38 ng/L with the average concentration of 27.60 ng/L, which is much lower than the surface water. However, the concentration is higher than some other study areas[9]. MLs are detected at 22.2% of the groundwater samples with the range from below the limit of quantification (BLQ) to 44.51 ng/L. DOC and CTC have the highest detection frequency, 88.9% and 44.4%, respectively, and with the range from BLQ to 22.06 ng/L and BLQ to 15.06 ng/L, respectively. TCs is also the main contaminant which is 100% detected with the concentration of 1.90 ng/L to 35.06 ng/L. Only 3 of 9 FQs has been detected with the concentration between BLQ to 36.30 ng/L. 7 of 8 SMs were found in the groundwater, their highest concentration was not greater than 1.60 ng/L. MLs were only detected at sites GW-19 and GW-27.

Figure. 3 The distribution of antibiotics in the groundwater
4. Conclusions

The antibiotics are ubiquitous in the soil and water environment. All the 25 kinds of antibiotics have been detected in the surface water in this study area. The order of average detection frequency is MLs > FQs > TCs > SMs. The concentration of antibiotics in drainage canals is higher than rivers. 15 of 25 kinds of antibiotics were detected in the groundwater. The detection frequency was lower than other study areas in China. The concentrations ranged from 2.75 ng/L to 114.38 ng/L with the average concentration of 27.60 ng/L. MLs and FQs were the main antibiotics detected in the shallow vadose zone. 22 and 20 kinds of 25 antibiotics were detected respectively in the sediment core of sewage irrigation area and groundwater irrigation area. The order of concentration of 4 categories of antibiotics in both cores was: FQs > TCs > SMs > MLs.

The antibiotics in the environment mainly came from the sewage which from the sewage treatment plants and livestock breeding farms which along the drainage canals. Transport of the contaminants via lateral recharge due to lack of seepage prevention measures, therefore, poses a potential threat to the soil-groundwater system. The measures to prevent canal banks from seepage were able to retard antibiotics transport into the soil and groundwater system via lateral recharge.

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6. References

[1] Li J L, Wang Y X, Zhang C X, et al. The source apportionment of polycyclic aromatic hydrocarbons (PAHs) in the topsoil in Xiaodian sewage irrigation area, North of China. Ecotoxicology, 2014, 23 (10): 1943-1950.
[2] Yang X F. Thought about the construction and management of Fenhe River irrigation area. Soil and Water Conservation Science and Technology in Shanxi, 2012, 3: 28-30 (in Chinese).
[3] Zhang C X, Liao X P, Li J L, et al. Influence of long-term sewage irrigation on the distribution of organochlorine pesticides in soil-groundwater systems. Chemosphere, 2013, 92 (4): 337-343.
[4] Liao X P, Zhang C X, Yao L L, et al. Sorption behavior of nonylphenol (NP) on sewage-irrigated soil: kinetic and thermodynamic studies. Science of the Total Environment, 2014, 473-474: 530-536.
[5] Li J L, Dong Y H and Sun Z X. Fate of antibiotics in the soil-groundwater system in sewage irrigation area. Proceedings of 44th Annual Congress of the International Association of Hydrogeologists, 2017.
[6] Azzouz A and Ballesteros E. Combined microwave-assisted extraction and continuous solid-phase extraction prior to gas chromatography-mass spectrometry determination of pharmaceuticals, personal care products and hormones in soils, sediments and sludge. Science of The Total Environment, 2012, 419: 208-215.
[7] Tong L, Huang S B, Wang Y X, et al. Occurrence of antibiotics in the aquatic environment of Jianghan Plain, central China. Science of the Total Environment, 2014, 497-498: 180-187.
[8] Luo Y, Xu L, Rysz M, et al. Occurrence and transport of tetracycline, sulfonamide, quinolone, and macrolide antibiotics in the Haihe River basin, China. Environ Sci Technol, 2011, 45 (5): 1827-1833.
[9] Hannappel S, Balzer F, Groeneweg J, et al. Incidence of veterinary drugs in near-surface groundwater below sites with high livestock density in Germany. Hydrologie Und Wasserbewirtschaftung, 2014, 58 (4): 208-220.