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Distribution, dynamics and determinants of antibiotics in soils in a peri-urban area of Yangtze River Delta, Eastern China

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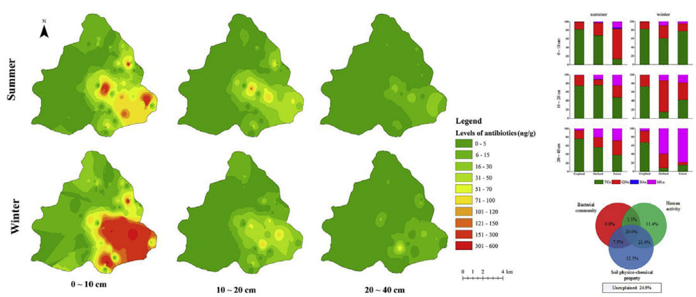
HIGHLIGHTS

- Antibiotics in soils were investigated in a typical peri-urban catchment of Yangtze River Delta, China.
- Antibiotic concentrations (i.e. chlortetracycline) in cropland soils were higher than those in orchard and forest.
- Land use intensity and structure significantly correlated with antibiotic concentrations ($p < 0.05$).
- Anthropogenic factors contributed more to soilcontamination by antibiotics.

GRAPHICAL ABSTRACT



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ABSTRACT

Antibiotics are increasingly recognized as anthropogenic contaminants in soils, and they can persist through a complex vicious cycle of transformation and bioaccumulation. In this study, we quantified 11 quinolones (QNs), 5 sulfonamides (SAs), 5 macrolides (MLs), and 4 tetracyclines (TCs) in soils at three soil layers (0–10, 10–20, 20–40 cm) in a typical peri-urban catchment in the Yangtze River Delta, Eastern China. The results showed that total antibiotic levels were significantly higher in cropland topsoil ($p < 0.05$) compared to orchards and forests ($p < 0.05$). Moreover, a significant seasonal variation for antibiotic concentrations in croplands' topsoil were observed in the summer (50.59 ± 84.55 ng/g) and winter (112.44 ± 140.58 ng/g). Chlortetracycline (15.30 ± 45.44 ng/g), enrofloxacin (0.43 ± 0.93 ng/g), sulfamethazine (0.05 ± 0.02 ng/g) and clarithromycin (0.03 ± 0.03 ng/g) were detected with the highest frequencies within TCs, QNs, SAs, and MLs, respectively. Concentrations of TCs, QNs, and SAs decreased with increasing soil depth. The concentrations of TCs, QNs, and SAs were significantly affected by the intensity of human activities. According to the results of redundancy analysis (RDA), anthropogenic effects on the distribution of antibiotics in soils in winter were so strong that they dwarfed the effects of environmental factors. In summer, human activities and their interactions with environmental factors were the dominant contributors to variations in soil antibiotics. In addition, the results of RDA suggested that soil pH and organic matter closely correlated with the levels of antibiotics, and *Actinobacteria* was the predominant contributor to the biodegradation of antibiotics in this study area.

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1. Introduction

Antibiotics are commonly and widely used for human health and animal growth (Kümmerer, 2009a, 2009b; Tasho and Cho, 2016). Between 2000 and 2010, global consumption of antibiotics increased by 36%, and China is one of the largest producers and consumers of antibiotics with an estimated production of 210,000 t per year (Li et al., 2015; Van Boeckel et al., 2014). Antibiotics cannot be completely adsorbed and metabolized by humans or other animals: approximately 16%–84% of antibiotics are excreted via urine and feces (Awad et al., 2014; Martinez, 2009). There is a concern that environmental input of antibiotics via land application of manure, effluent from municipal wastewater treatment, or irrigation with reclaimed water may increase antibiotic concentrations in the environment (Martinez, 2009). Furthermore, high concentrations of antibiotics in the environment can be associated with an increased presence of resistant bacteria, which is an important public health concern due to the prevalence of associated clinical infections (Zhu et al., 2017).

Previous studies have reported high concentrations of antibiotics in agricultural soils due to fertilization and irrigation (Christou et al., 2017; Pan and Chu, 2017a; Wu et al., 2015). For example, Zhang et al. (2015) reported that 53,800 tons of antibiotics were excreted by humans and animals in China, with 54% accumulating in soil compartments. In addition, antibiotics persist in soil environments over the long term with continuous loading of antibiotic pollutants (Rahman et al., 2018; Riaz et al., 2018). Indeed, in a field with a 13-year history of manure application, the mean concentrations of selected antibiotics in soils increased by at least 120% (Li et al., 2017). Residual antibiotics in soils can inhibit the growth of crop roots and soil microorganisms. Meanwhile, they can also lead to abundant antibiotic resistance genes (ARGs) and a diverse array of resistant bacteria, seriously threatening the security and stability of soil ecosystems (Kümmerer, 2009b; Liang et al., 2017; Zhao et al., 2017). Moreover, antibiotic residues in soils due to agricultural practices may represent an enhanced threat to human health via ingestion of contaminated food (Pan and Chu, 2017a; Tasho and Cho, 2016; Wei et al., 2016).

Antibiotic compounds have different persistence and transportation modalities and abilities in soils, including sorption, degradation, and leaching (Kümmerer, 2010; Pan and Chu, 2017a). The environmental fate of antibiotics in soils is more likely to be affected by the physicochemical properties of antibiotics (Tolls, 2001). Tetracyclines are associated with several orders of magnitude higher sorption ability than other antibiotics (Rabølle and Spliid, 2000; Kuppusamy et al., 2018). For example, the soil adsorption coefficient (K_d) of sulfachloropyridazine ranges from 0.90 to 1.80 (1/kg) in clay loam, while chlortetracycline exhibits the highest adsorption ability with K_d ranging from 1280 to 2386 (1/kg) (Pan and Chu, 2017a). The sorption, migration, and degradation of antibiotics in soils is significantly affected by soil pH, soil texture, metals ions, organic matter, rainwater pH, and rainfall duration (Pan and Chu, 2017b; Qin et al., 2017; Zhang et al., 2014). For tetracyclines, cation exchange is an important mechanism for their adsorption in clay minerals, which is depended on the charge of both antibiotic compounds and clay minerals (Pils and Laird, 2007). Tetracycline antibiotics are positively charged in strongly acidic solutions indicating neutralize negative charge sites on clay surface, while they are anionic under alkaline conditions which will be repulsed from clay surfaces (Aristilde et al., 2010; Figueroa et al., 2004). Additional, the charge of clays can also vary with pH, and inner-sphere sorption is the main mechanism of adsorption for tetracyclines antibiotics on variable charge clay minerals (Zhao et al., 2011). It was reported that the presence of Ca^{2+} and Mg^{2+} can strongly account for the formation of inner-sphere complexes with tetracycline antibiotics, which can influence antibiotic retention behaviour on mineral surfaces (Aristilde et al., 2016; Dolui et al., 2018).

Studies have also found that there are complex relationships between antibiotic concentrations and bacterial communities in soils. Soil bacterial communities are significantly changed under the selection pressures of antibiotics due to the effects of antibiotics on microbial activity and biomass (Hammesfahr et al., 2008; Thiele-Bruhn and Beck, 2005). Certain bacteria can also degrade antibiotics (Liao et al., 2016a). However, there is a lack of clarity vis-a-vis the differential contribution of anthropogenic and environmental factors on the persistence and distribution of antibiotics in soils.

In recent decades, rapid urbanization and agricultural development have greatly affected the soil environment in the Yangtze River Delta (YRD), China. To meet increasing demand for organic produce, long-term and heavy application of animal manures in agricultural fields has occurred, especially in peri-urban areas due to multiple economic and social benefits. However, this cultivation may also elevate the contamination of soils with antibiotics. Most urban wastes subsequently decompose in peri-urban areas, and many ecosystem services are supplied by peri-urban soils such as food supply, soil carbon sequestration, and water conservation. Contamination of soil by antibiotics risks undermining these ecosystem services. Illuminating the spatial and seasonal variation of soil antibiotics in peri-urban areas could promote the sustainability of soil and the delivery of ecosystem services. In a typical peri-urban catchment of YRD, soil antibiotics and determinants thereof were quantified and explored. Specifically, in this study, we aimed to: (1) compare the composition and concentration of soil antibiotics across different land use types; (2) explore the spatial distribution of soil antibiotics and its seasonal variation in peri-urban areas; (3) identify the main determinants of spatial and temporal variations in soil antibiotics.

2. Materials and methods

2.1. Study area

The Zhangxi catchment (29°45′–29°51′ N, 121°13′–121°20′ E), located in a rapidly urbanizing area of Yangtze River Delta, Eastern China, was selected as the study area (Fig. 1). The catchment has an area of 91.6 km^2 and is located in the typical peri-urban area of Ningbo city. It has a subtropical monsoon climate, with an annual mean cumulative precipitation of 1480 mm. Mean monthly temperature is highest in July (28.0 °C) and lowest in January (4.7 °C). The soil layer in the catchment is shallow (mean of ca. 30 cm) and is typically characterized by a silt loam topsoil with a sandy loam subsoil. The main land use types in the catchment are forests, cropland, orchards, residential areas, a river, and a reservoir. Cropland (fritillaria, vegetables, fruit) is mainly distributed along the river channel. Organic fertilizer or manure is widely applied to cropland in October of each year; and some orchards are also fertilized in this way.

The study area was classified into four sub-catchments (SC1, SC2, SC3, and SC4) with an ‘obvious human activities’ gradient. SC1 is essentially a natural ecosystem, with forest coverage of 96.3%, while there are intensive human activities in SC4 with a high proportion of cropland and villages (35.8% and 10.3%, respectively); see Table S1.

2.2. Soil sampling and characterization

A total of 82 sampling sites were selected in the catchment in July 2016 (summer) and January 2017 (winter). The daily average