



**HAL**  
open science

# Fate and transport of tetracycline and ciprofloxacin and impact on nitrate reduction activity in coastal sediments from the Seine Estuary, France

Chen Chen, Anniet M. Laverman, Céline Roose-Amsaleg, Garance Regimbeau, Khalil Hanna

## ► To cite this version:

Chen Chen, Anniet M. Laverman, Céline Roose-Amsaleg, Garance Regimbeau, Khalil Hanna. Fate and transport of tetracycline and ciprofloxacin and impact on nitrate reduction activity in coastal sediments from the Seine Estuary, France. *Environmental Science and Pollution Research*, 2023, 30, pp.5749-5757. 10.1007/s11356-022-22564-1 . hal-03770462

**HAL Id: hal-03770462**

**<https://hal.science/hal-03770462>**

Submitted on 6 Oct 2022

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



# Fate and transport of tetracycline and ciprofloxacin and impact on nitrate reduction activity in coastal sediments from the Seine Estuary, France

Chen Chen<sup>1,2</sup> · Annet M. Laverman<sup>1</sup> · Celine Roose-Amsaleg<sup>1</sup> · Garance Regimbeau<sup>1</sup> · Khalil Hanna<sup>2</sup>

Received: 3 June 2022 / Accepted: 11 August 2022

© The Author(s), under exclusive licence to Springer-Verlag GmbH Germany, part of Springer Nature 2022

## Abstract

Fluoroquinolones and tetracyclines are frequently detected antibiotics in aquatic sediments. In this study, the transport of ciprofloxacin (CIP) and tetracycline (TET) was investigated in sediments from the Seine Estuary (France), under nitrate reducing conditions. Dynamic flow experiments showed that although TET and CIP strongly interacted with the sediment components through adsorption and (bio)-chemical transformation, they kept their antimicrobial activities. Less nitrate reduction was observed during the first period of breakthrough, while TET and CIP were absent in the column effluent. Batch experiments with freeze-dried vs fresh sediments showed that adsorption and abiotic degradation are the major removal processes, while microbe-driven transformation is of less importance. Whereas TET is to a large extent chemically transformed and little adsorbed in the sediment, CIP was less transformed and more adsorbed, most likely due to the great reactivity of TET with redox-active mineral surfaces. Our findings show the strong capacity of natural sediment to retain and transform antibiotics, while still maintaining their antimicrobial activity or inhibitory effect of nitrate reducing activity.

**Keywords** Antibiotic · transport · Antimicrobial activity · Nitrate reduction activity · Mobility · Sediment

## Introduction

Fluoroquinolones (FQs) and tetracycline (TCs) are widely used classes of antibiotics in human and veterinary medicine for treatment and prevention of various infectious diseases (Sarmah et al. 2006). On average, 60% of the administered doses of tetracycline (Kühne et al. 2000) or quinolones (Vree et al. 1986) are excreted via urine and faeces. These un-metabolized antibiotics can enter the aquatic environment, be transported by water (Kümmerer 2008) and ultimately deposited in soil or sediment (Agunbiade and Moodley 2016; Gibs et al. 2013; Luo et al. 2011; Zhou et al. 2011). Sediments can thus become

a major sink for antibiotics, which may increase the risk of the emergence of antibiotic resistant bacteria and the spread of resistance genes.

Monitoring studies of FQs and TCs have been more frequently investigated in the water phase than the sediment one (Harrower et al. 2021). For example, ciprofloxacin (CIP), one of the most used FQs, has been found at levels up to 569  $\mu\text{g Kg}^{-1}$  in sediment (Dinh et al. 2017); tetracycline (TET) concentration reached up to 72.9  $\mu\text{g Kg}^{-1}$  (Yang et al. 2010). For this reason, the fate and mobility of antibiotics in riverine and estuarine sediments are of growing concern. Sorption to sediment constituents, e.g. metal-oxides, clays and organic matter, is a major process affecting the fate and migration of antibiotics in nature (Conde-Cid et al. 2020; Pavlović et al. 2017; Xu et al. 2021). Moreover, redox reactions may occur on environmental surfaces where electron transfer processes may transform the adsorbed compounds. Among these redox active surfaces, Fe and Mn oxides are the most abundant reactive minerals typically present in sediment systems (Martin et al. 2015; Wang et al. 2016; Zhang and Huang 2005). Depending on the molecule properties, half-life of abiotic degradation ranges from a few days to several months (Boxall 2008).

Responsible Editor: Philippe Garrigues

✉ Khalil Hanna  
khalil.hanna@ensc-rennes.fr

<sup>1</sup> Univ Rennes, CNRS, ECOBIO UMR 6553, F-35000 Rennes, France

<sup>2</sup> Univ Rennes, Ecole Nationale Supérieure de Chimie de Rennes, CNRS, ISCR – UMR6226, F-35000 Rennes, France

Furthermore, microbe-driven degradation may play a role in natural attenuation or environmental degradation of antibiotics (Wang et al. 2019). Degradation of tetracycline is one of the TET antibiotic resistance mechanisms. Microorganisms harboring the *tet(X)* gene, encoding tetracycline-degrading monooxygenase are capable of TET degradation (Ghosh et al. 2009). The biodegradability of TET and quinolones, such as ofloxacin and CIP, has been shown to be improved in the presence of carbon sources suggesting co-metabolism (Alexy et al. 2004; Pan et al. 2018). Biodegradation of CIP by consortia or pure bacterial culture has been shown mainly by bacteria originating from waste water treatment plants or conventional activated sludge (Rusch et al. 2019). The biodegradation efficiency of antibiotics by single microorganisms depends on temperature, pH, carbon source, and inoculum, whereas in environmental systems such as soils or sediments, adsorption and bacterial community structure could be the main influencing factors (Shao and Wu 2020).

Although different abiotic and biotic processes control the fate of antibiotics in such systems, knowledge about the behavior of antibiotics in more complex environments such as coastal sediments is limited. Most of the previous published works have investigated abiotic or microbial degradation of antibiotics separately, and under static conditions (e.g. suspensions), and little is known about their fate and (bio)-chemical transformation under anoxic flow-through conditions. Among the environmental processes naturally occurring in sediment, nitrate reduction is an anaerobic reaction of great importance as it allows a 50% decrease of nitrate pollution of coastal sediments (Galloway et al. 2004). Knowledge on the impact of antibiotics on the nitrate reducing activity of microbes in the coastal sediments is scarce. Therefore, it is important to investigate dynamic flow transport of the most frequently detected antibiotics in nature, coupled to the assessment of their antimicrobial activities within intact real sediment.

In the present work, the fate and mobility of TET and CIP in sediments sampled from north bank of the Seine Estuary, France, was investigated in packed reactors under controlled flow conditions. The sediment sample was first characterized by X-ray Diffraction (XRD), Inductively Coupled Plasma–Optical Emission Spectrometry (ICP-OES), laser particle size analyzer and elemental C, H, N, S analyzer. The flow through reactors (FTRs) were used to study the mobility of TET and CIP in sediment under nitrate reducing conditions. Inflow solutions of TET and CIP were injected in sediment reactors at a constant flow rate. The inflow solutions contained NaCl and NaHCO<sub>3</sub> to emulate natural coastal environment, and nitrate to determine the nitrate reducing activity. The antimicrobial activity of antibiotics within the sediment was monitored through the determination

of nitrate reduction and nitrite production rates using a Gallery™ Plus Discrete Analyzer (Thermo Fisher). Batch experiments with fresh vs freeze-dried sediments were carried out to evaluate respectively biotic and abiotic degradation processes of antibiotics, because freeze-drying is known to minimize bacterial activity (Champagne et al. 1991). Liquid chromatography (LC) combined with UV and/or mass spectrometry (MS) was used to quantify the antibiotics and to identify potential degradation byproducts. The present work will improve the understanding of the behavior of TET and CIP in coastal sediments, and thus has important implications in assessing ecotoxicological risks related to these emerging compounds in the environment.

## Material and methods

### Sediment sampling and characteristics

Sediment samples were collected from the Seine Estuary (Saint-Vigor-d'Ymonville, France) in September 2020 (Fig. S1). All the sediments collected were composed of fine-grained anoxic mud with a dark gray appearance. The sediment was then stored in aluminum coated containers at a 4°C fridge prior to use. The pH of fresh sediment lied at  $8.04 \pm 0.03$  (average of 10 samples).

Elemental analyzer (Shimadzu TOC V-CSH analyzer) showed that the sediment had an average total organic carbon (TOC) content of 1.49%, and total nitrogen content (TON) of 0.13%. Laser particle size (Malvern) analysis showed the natural sediment had an average particle size of  $56 \pm 1\mu\text{m}$ , with a high proportion of  $70 \pm 1\%$  of 2–63 $\mu\text{m}$  size (classified as slit based on ISO 14688-1), and a minor proportion of  $5 \pm 1\%$  below 2 $\mu\text{m}$  size (classified as clay based on ISO 14688-1). According to XRD analysis, the sediment was mainly composed of quartz with traces of metal oxides (not shown).

Acid digestion of the sediment followed by ICP-OES measurements showed high concentrations of Ca with respect to Al, Fe, and Mg. Cu, Ni, Cd, and Co were below the detection of the ICP-OES. A sequential extraction procedure was also conducted according to a previous reported method (Ure et al. 1993). In the first step, the acid-soluble fraction (carbonate and exchangeable fraction) was extracted with HCl 0.1mM. HCl (10mM, pH2) was then used in the second step to digest metals linked to the amorphous fraction. Total acid digestion was finally carried out using 50% aqua regia (3:1 HCl: HNO<sub>3</sub>) to completely remove total metal content. The supernatant was analyzed by ICP-OES. The characteristics of the Seine river sediment are shown in Table S1.

## Flow-through reactors

The setup of the flow-through reactors (FTR) was designed to investigate the effect of natural sediment on breakthrough behavior of selected antibiotics (TET and CIP) when continuously supplied with a defined input solution at a low flow rate. The FTR system consists of 2 square blocks placed on and under a plexiglass column. Two filters were placed on the inner face of the blocks: a thick glass fiber filter (PALL) to homogenize the inlet of the solution and a PVDF filter (Millipore) with 0.2 μm porosity to prevent bacteria from entering and exiting the reactor. A peristaltic pump (Gilson minipuls3) supplied the solution continuously into the reactor. The tubes connecting the bottles to the reactors were made of Tygon, to avoid absorbing solvents. A scheme of FTR is shown in Fig. S3 and described in more detail in Laverman et al. (2006).

Briefly, 38 ± 2 g of fresh natural sediment (well saturated) was packed into plexiglass columns of 4.2 cm internal diameter, 2 cm height, and 27.7 ml internal volume. After packing to a uniform bulk density (1.37 ± 0.07 g cm<sup>-3</sup> for fresh sediment), the column was supplied continuously upward with a synthetic input solution at a constant flow rate (2 ml per hour). The basic input solutions were sterile saline water (1% NaCl, 2.4 mM NaHCO<sub>3</sub>) supplemented with 5 mM of nitrate (KNO<sub>3</sub>) at pH 8, flushed with nitrogen to remove oxygen in the air. The water content of the sediment in FTR was relatively constant with an average value 44% (average of 20 samples). The pore volume of FTR column (PV=16.8 mL) was estimated by weight difference between the fully saturated and freeze-dried sediment. The flow through experiments were duplicated for each experimental set: control group (no CIP or TET), TET (4.5 μM TET), CIP (3.0 μM CIP), and MIX (5.8 μM TET and 0.8 μM CIP). The tested concentrations of TET and CIP were chosen based on the definition of break points between sensitive and resistant (9.0 μM TET and 3.0 μM CIP) for bacteria, according to the *EUCAST and CLSI-potency NEO-SENSITABS™ User's Guide 2013*, when used individually, and based on Predictive Environmental Concentration according to DeVries and Zhang (2016) when used as mixture.

Tracer experiments using bromide (Br<sup>-</sup>) showed classical shape, *i.e.* sigmoidal shape with no big tailing, as reported in a previous work (Pallud et al. 2007). As expected, a small bed length with respect to column diameter suggests that both advection and diffusion may occur in the FTR system. Peclet number ( $P_e$ ) can be then calculated using the equation  $P_e = \nu L / D$ , where  $\nu$  is the water velocity (cm s<sup>-1</sup>),  $L$  is the bed length of the FTR column, and  $D$  is the molecular diffusion coefficient of tracer. The water velocity  $\nu$  was obtained via  $\nu = q / \theta$ , with  $q$  the Darcy flux (cm s<sup>-1</sup>) and  $\theta$  the porosity. If we take the molecular diffusion for the bromide ion (2.0 ± 0.2 10<sup>-5</sup> cm<sup>2</sup> s<sup>-1</sup>) (Bowman 1984; Shackelford and Daniel

1991; Willingham et al. 2004),  $P_e$  lies at around 4, thereby underscoring the occurrence of diffusion processes.

## Batch experiments and analyses

Different extraction methods were applied to TET ([1 M NaCl: 1 M oxalic acid: ethanol (25:25:50)]) or CIP ([2% ammonia in methanol + 2% formic acid in methanol + pure methanol]). The detailed operation steps are given in the supporting information. The antibiotic extraction efficiency from sediment was tested to be 71% ± 4% for TET, and 80% ± 3% for CIP.

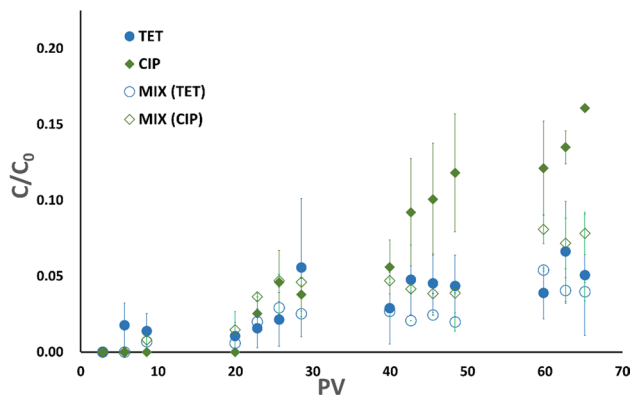
Fresh (3.6 g) or freeze dried (2.0 g) sediment and 25 mL TET (4.1 μM) or CIP (3.0 μM) and nitrate (5 mM KNO<sub>3</sub>) containing sterile saline water (171.1 mM NaCl, 2.4 mM NaHCO<sub>3</sub>) were mixed in 50 mL tubes. The tubes were flushed with nitrogen, in order to simulate the same condition as FTR. The tubes were then covered by aluminum and incubated in an automatic shaker, at 250 rpm under room temperature. After shaking for a certain time (2 min, 1 week, 2 weeks, and 3 weeks), the tubes were centrifuged at 4500 rpm for 20 min, and the supernatants were analyzed by UPLC to measure and calculate the un-transformed amounts of CIP and TET. Subsequently, the pellet (solid phase) left in the tubes were freeze dried and extracted by the specific extraction method of TET or CIP described in supporting information. All treatment and analysis were done in triplicate.

CIP and TET aqueous concentrations were determined using an ultra-performance liquid chromatography (UPLC Hclass Waters) equipped with a UV detector and a reversed-phase C18 column (250 mm×4.6 mm i.d., 5 μm). The injection volume of UPLC Hclass was set to 50 μL for each analysis. Two different mobile phases were applied to UPLC for CIP and TET determination. Mobile phase A was an aqueous solution containing 90% ultra-pure water, 10% acetonitrile, and 0.1% formic acid. Mobile phase B was 0.1% formic acid in acetonitrile. The volume fraction of solvent B was 10% for the analysis. The mobile phase flow rate was set to be 0.4 mL/min. The detection limit of CIP and TET were respectively 0.03 μM and 0.05 μM.

## Results and discussion

### Mobility behavior of TET and CIP in sediment-packed columns of FTR

Breakthrough experiments of TET and CIP were conducted at pH 8 (buffered by the presence of NaHCO<sub>3</sub>) and a low flow rate (33 μl min<sup>-1</sup>) to avoid kinetic limitations under flow-through conditions (Fig. 1). For all systems, the out-flow pH changed very slightly, and stayed at 8 ± 0.1. The



**Fig. 1.** CIP and TET breakthrough curves (BTC) from FTR experiments. Experimental conditions: pH 8 (2.4 mM NaHCO<sub>3</sub>), nitrated saline water (1% NaCl, 5mM KNO<sub>3</sub>), and flow rate 33  $\mu\text{L min}^{-1}$ . TET and CIP inflow concentrations ( $C_0$ ): TET (4.5  $\mu\text{M}$ ), CIP (3.0  $\mu\text{M}$ ), and MIX (5.8  $\mu\text{M}$  TET and 0.8  $\mu\text{M}$  CIP). The error bars are standard deviations for duplicates.

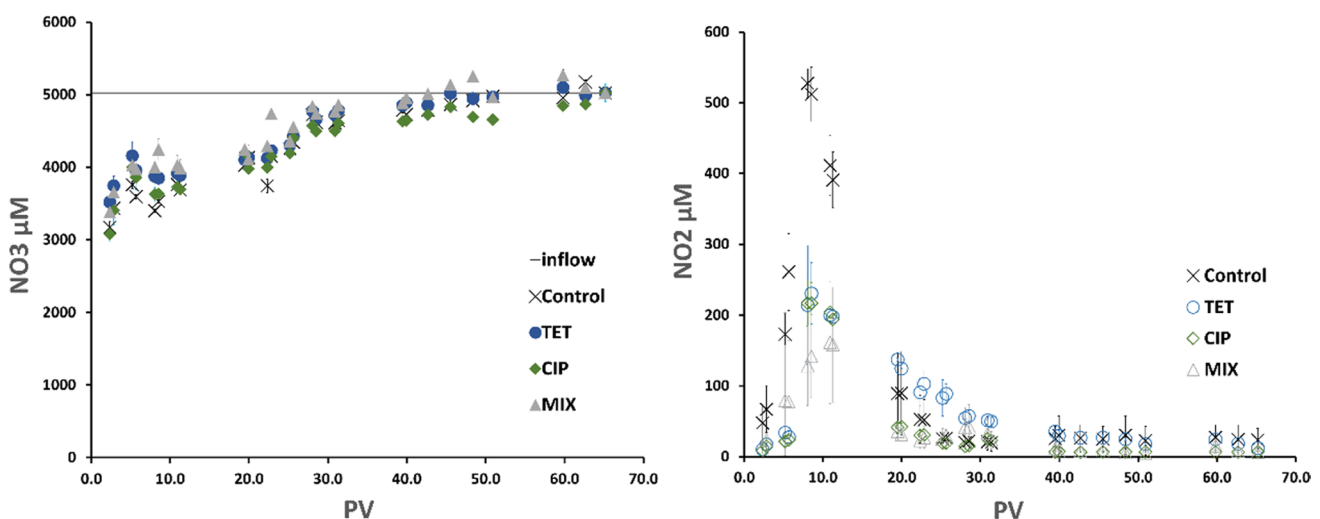
solute breaks out at around 25 pore volumes (PV), for both TET and CIP, and regardless of the injection scenario (single or binary). Then, the outflow concentration increases gradually with a long tailing, but does not exceed  $C/C_0 \sim 0.15$ , even after an injection of 75 PV (about 600 h under the current flow rate). This suggests that the sediment has a great capacity to remove TET or CIP from aqueous phase, through for instance sorption to sediment constituents and/or (bio)-chemical transformation.

To determine the mass balance, an extraction of the sediment after the breakthrough experiment was conducted and compared to the removed amount calculated from the

breakthrough curve (BTC) of each compound. Mass balance calculations indicated that  $51 \pm 2\%$  of removed TET and  $32 \pm 3\%$  of removed CIP were not recovered independently on the injection mode (single or mixture). This suggests molecular transformation of TET and CIP within the sediment during the dynamic flow experiments.

Previous reports have shown that microbial abundance and diversity within sediments can be altered by the presence of antibiotics in inflow solution (Fan et al. 2020; Girardi et al. 2011; Liu et al. 2016). To evaluate the impact of TET and CIP on the nitrate reducing activity within the sediment, the BTC of nitrate and nitrite were also determined versus PV (Fig. 2). Alteration of the nitrate reduction and nitrite production activity are mainly observed during the first 12 PVs of the breakthrough experiment. As shown in Fig. 2 and Table S2, less nitrate flowed out from the control group than from those with addition of antibiotics. This indicates that more nitrate was consumed in the sediment without antibiotics, i.e. the control group ( $1458 \pm 202 \mu\text{M}$ ) compared to the antibiotic amended sediments (TET  $1135 \pm 182 \mu\text{M}$ , CIP  $1293 \pm 282 \mu\text{M}$ , MIX  $1085 \pm 268 \mu\text{M}$ ), and thus, nitrate reduction activity in the sediment during this stage was inhibited. This inhibition is approximately 30% for TET and 15% for CIP compared to the control test. This inhibition was only observed during the first period of the flow experiment (up to 12 PV).

The intermediate nitrite production also shows difference, nitrite production in the control group ( $299 \pm 190 \mu\text{M}$ ) was 2–3 times higher than that in antibiotic added groups (TET  $117 \pm 101 \mu\text{M}$ , CIP  $113 \pm 102 \mu\text{M}$ , MIX  $98 \pm 58 \mu\text{M}$ ). For the sediments exposed to TET the nitrite production remains higher throughout the experiment (see Fig. 2). Overall, the



**Fig. 2.** Nitrate and nitrite breakthrough curves. Experimental conditions: pH 8 (2.4 mM NaHCO<sub>3</sub>), nitrated saline water (1% NaCl, 5mM KNO<sub>3</sub>), and flow rate 33  $\mu\text{L min}^{-1}$ . TET and CIP inflow concentra-

tions: TET (4.5  $\mu\text{M}$ ), CIP (3.0  $\mu\text{M}$ ), and MIX (5.8  $\mu\text{M}$  TET and 0.8  $\mu\text{M}$  CIP). The error bars are standard deviations for duplicates.

lower nitrate reduction and nitrite production rates in the sediments exposed to the antibiotics indicate an inhibition of the microbial activity. Even though TET concentrations are low in the outflow, its presence has impacted nitrate reducing and nitrite producing activity. Similar experiments showed no inhibition in river sediments, though a TET concentration up to 22.5  $\mu\text{M}$  (Roose-Amsaleg et al. 2013). Other studies, however, showed significant decreases of denitrification rates from 30% at 1.7  $\mu\text{M}$  TET to 70% at 17  $\mu\text{M}$  TET in soil samples (Shan et al. 2018), or 75% at 22.5  $\mu\text{M}$  TET in sediment samples (Zhang et al. 2019). These differences in effect of TET on nitrate reduction could be due to a more adapted microbial community, i.e. presence or absence of resistance, or sediment characteristics impacting the availability of TET.

The effect of CIP (quinolones) on nitrate reduction activity is in line with observations in river sediments, with a partial inhibited nitrate reduction rate by 40% in presence of 200  $\mu\text{M}$  flumequine (Yan et al. 2013). Elevated CIP concentrations (90  $\mu\text{M}$ ) were shown to inhibit nitrate reduction rates up to 65% in active sludge (Yuan et al. 2021), and 10% at 6  $\mu\text{M}$  CIP in WWTP sludge samples (Yi et al. 2017).

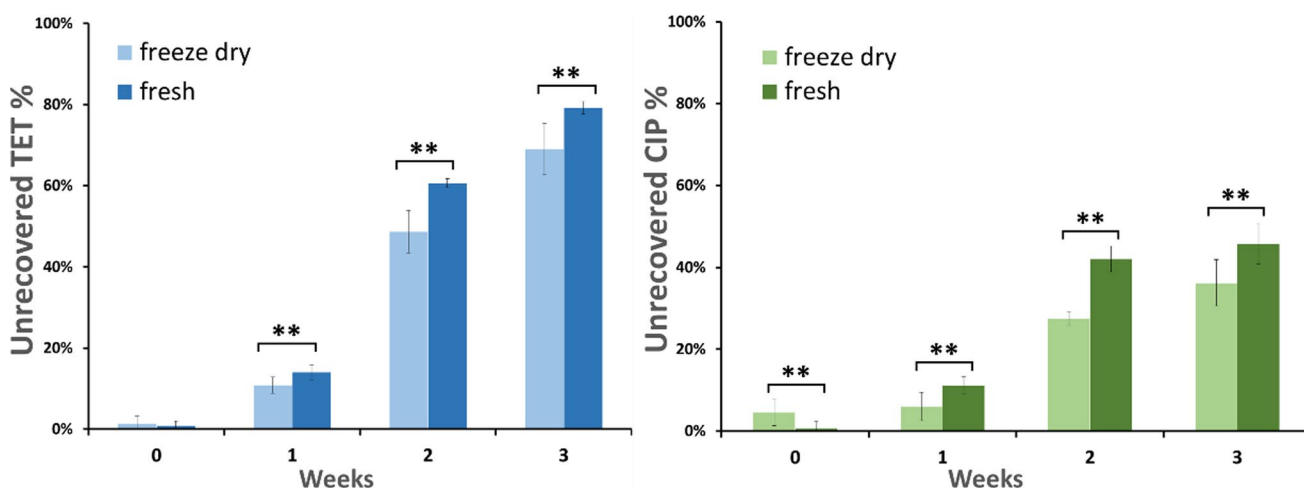
In the treatment with both TET and CIP (MIX), no significant difference compared to the single application was observed regarding the nitrate reduction and nitrite production rates. After injection of  $\sim 50$  PV, no inhibition was observed as nitrate reached complete breakthrough and no nitrite was formed (Fig. 2). The reaching of complete breakthrough of nitrate indicates that nitrate reduction activity has ceased. This could be attributed to the leaching of organic carbon (see Fig. S4), as the same behavior was observed in all systems including the control. The DOC in the outflow of the reactor is the result of (sediment) organic carbon

degradation due to microbial activity, including nitrate reduction. The decrease in DOC with time is most likely due to the fact that the available organic carbon decreases over time and no additional carbon was added during the experiment. The quick decrease in DOC observed over the first 12 PVs is consistent with the period in which denitrifiers were more active (as shown in Fig. 2). Indeed, a decrease in organic carbon within the sediment may affect the microbial and nitrate reducing functioning as organic carbon is required for nitrate reducing activity (Payne 1973).

### Transformation of TET and CIP under batch conditions

To check whether the molecular transformation of TET or CIP may take place in the investigated sediment, batch experiments were conducted over 3 weeks in aqueous suspension under similar conditions as for reactor experiments at pH 8. Since freeze-drying is known to inhibit the bacterial activity (Champagne et al. 1991), biotic (microbe-driven process) and abiotic (mineral-induced reactions) degradations can be assessed through comparison of removal amounts in fresh vs freeze-dried sediment.

As observed in the FTR system, strong adsorption of TET and CIP can be achieved for both fresh and freeze-dried sediments (Fig. 3). Extraction was then conducted at different reaction times to determine the mass balance, and thus to calculate the amount of transformed (unrecovered) compound (Fig. 3). This amount increased with reaction time, and is slightly higher for the fresh sediment, suggesting the occurrence of both abiotic and biotic degradation in the sediment.



**Fig. 3.** Comparison of unrecovered ratio of TET and CIP to total aqueous removal amount, in the presence of freeze-dried sediment and fresh sediment. *P*-value statistical significance testing: when

set  $\alpha=0.05$ , \*\* represents  $P<0.05$  (a significant difference could be stated between two tested groups). The error bars are standard deviations ( $n=3$ ).

After three weeks of reaction time, around 70% of TET and 40% of CIP were transformed. In the fresh sediment, a slight increase in transformation was observed, compared to the freeze-dried sediments. If we suppose that this difference, though slight, can be attributed to biological-driven degradation, we can determine the contribution of each process in the total removal of compound in batch experiments (Fig. S5). In the present work, aluminum foil was used to prevent photolysis, nitrogen gas flush was applied to inhibit aerobic biodegradation, and consequently anaerobic microbes like denitrifiers could potentially contribute to the biodegradation of TET and CIP. The biological-driven degradation for both TET and CIP was approximately 10%, confirming the minor contribution of this process. Different works using different sediment and soil systems reported different biodegradation rates for CIP or TET, thereby highlighting the key role of sediment characteristics and microbial community structure in determining the antibiotic removal. For instance, higher biological degradation in sediments/soils for TET was previously reported (Chang and Ren 2015; Pan and Chu 2016). For example, Chang et al. (2015) reported 79% decrease of TET in natural sediments, with 6.8% in autoclaved sediments, representing the abiotic transformation. Pan and Chu (2016) found that after 21 days of anaerobic incubation, 46.8% of total TET loss in non-sterilized soil versus 24.4% in a sterilized group. Comparable to the 10% biotic transformation in the investigated coastal sediments, low biodegradation rates were previously found for CIP. Zhang et al. (2012) showed that 13% of CIP can be biodegraded whereas Thuy and Loan (2014) found only 5% of total CIP could be removed in sterile vs non-sterile sediment system.

Overall, the results of the current study suggest that adsorption and abiotic degradation are the predominant processes for the removal of both TET and CIP, probably due to the characteristics of the investigated sediment.

### Difference in TET and CIP behavior within the sediment

Although the mass balance showed that CIP is more adsorbed and TET is more chemically transformed within the sediment, the affinity of both compounds to the sediment can be considered similar (i.e. sum of adsorption and chemical transformation is close) (see Fig. S5). It is known that the fate of antibiotics is often tied to their affinities to organic matter (Sithole and Guy 1987; Tolls 2001) and mineral particles (Nowara et al. 1997; Zhang et al. 2010) of sediments.  $\pi$ - $\pi$  electron donor-acceptor interactions, electrostatic interactions, H-bonding, and hydrophobic interactions, and surface complexation seem to be the most prominent mechanisms for their binding with sediment minerals and organic matter (Zhu et al. 2004). These interactions are

mainly affected by pH, sediments properties, and structural characteristics of the target compounds. Fluoroquinolones such as CIP are electron donor-acceptor compounds (Vasudevan et al. 2009) with the piperazinyl group serving as the electron donor and carboxylic group as the electron acceptor in the neutral and zwitterion forms (Fig. S6a). TET contains phenolic and carboxylic groups as the electron acceptor and the N-group as the electron donor, and has three  $pK_a$  (Fig. S6a). In the present work, the investigated sediment has a stable pH at 8, which could result in certain pH-dependent speciation of TET and CIP. As shown in Fig. S6b, both CIP and TET exist under zwitterion form at pH 8, which could be adsorbed onto charged mineral surfaces (Vasudevan et al. 2009; Zhao et al. 2012). The organic matter can also improve the total removal of compounds through adsorption process. For instance,  $95 \pm 5\%$  of oxytetracycline and  $30 \pm 10\%$  of tylosin were found removed by a sand-based soil with a TOC at 1.4% (Rabølle and Spliid 2000), whereas high TET adsorption to a marine sediment has been attributed to natural organic matter, though the investigated sediment contained only 1.3-1.9% of TOC (Xu and Li 2010). In the present work, we can suppose that 1.5% of sediment organic carbon may contribute to the total sorption of TET and CIP. Other works investigated the adsorption of antibiotics onto a sediment containing a similar organic content (1% TOC), and found high removal of ibuprofen (54%) and sulfamethoxazole (55%) (Banzhaf et al. 2012). However, these studies did not investigate the contribution of microbial activity in total removal of target compounds.

In the case of redox active minerals (e.g. Fe and Mn-oxyhydroxides), compound sorption may be followed by an electron transfer process resulting in the concomitant oxidation of adsorbed compound and reduction of surface-bound metal (Martin et al. 2015, Zhou et al. 2019). In the present work, the sediment contains non-negligible amounts of Fe and Mn: 7.91mg of Fe and 0.37mg of Mn per gram of freeze-dried sediment (Table S1). According to the sequential extraction method, most of Fe and Mn may likely exist under crystallized Fe and Mn-oxyhydroxides forms (Fig. S2). Although the Fe/Mn speciation in the sediment still needs more investigation, we can suppose that the reactive minerals such as Fe and Mn-oxyhydroxides could contribute to the chemical degradation of CIP and TET.

The higher CIP adsorption compared to TET, coupled to the higher chemical degradation of TET compared to CIP, may be related to the binding mechanisms and kinetics as well as the redox potential of each compound. Our previous work showed that weaker binding of phenolic compounds is more energetically favorable than the surface complexation of polyfunctional carboxylated compounds (e.g. CIP), and may enable higher removal rate with minerals (Jia et al. 2021). Therefore, we suppose that interactions of TET with mineral surfaces are faster than with CIP, enabling higher

oxidation rates. Furthermore, TET can also be transformed by hydrolysis at pH higher than 7 (Loftin et al. 2008). No potential by-products using LC/MS could be detected in the current study, probably because of the very low concentration of byproducts and/or their strong binding to sediments constituents. Taken together, these findings showed that the coastal sediment has a great capacity to remove both TET and CIP through adsorption and chemical degradation under our experimental conditions.

## Conclusions

Our study showed that coastal sediment could contribute to affect the mobility of TET and CIP, through adsorption and degradation processes, both under static and flow-through conditions. Chemical-driven transformation accounts for the largest proportion in TET/CIP removal with respect to biological process. This is likely due to the sediment composition and characteristics. TET is less adsorbed (~20%) but more chemically transformed (~70%) in sediment than CIP (~54% adsorption and ~36% transformation). Greater reactivity of TET with redox-active mineral surfaces under nitrate reducing conditions may explain its higher degradation efficiency in the sediment. Dynamic flow experiments showed that simultaneous injection of CIP and TET did not alter the mobility behavior of antibiotic or nitrate with respect to the single system. Although TET and CIP strongly interacted with the sediment components through sorption and (bio)-chemical transformation, they keep their antimicrobial activities. Indeed, inhibitory effect on the nitrate reducing activity was observed, despite the absence of TET and/or CIP in the outflow solution. This impact on the microbial growth and activities may also explain the low contribution of microbe-driven mechanism. The present work showed that assessments of the environmental risks of antibiotics must consider all physiochemical and biochemical interactions with the surrounding media, and not only their dissolved concentration in aquatic systems. These findings have, therefore, important implications in accurately predicting the fate and mobility of these emerging compounds in nature. Further investigations should focus on the assessment of the antimicrobial activities of transformation products of antibiotics in coastal sediments, and their impact on the biogeochemical cycle of nitrogen.

**Supplementary Information** The online version contains supplementary material available at <https://doi.org/10.1007/s11356-022-22564-1>.

**Acknowledgements** The authors acknowledge the ECOCHIM platform of the Rennes University for assistance with the nitrate and nitrite analysis. We are also grateful for the assistance of Isabelle Soutrel (LC/MS) and Mathieu Pasturel (XRD analysis).

**Author contribution** AML, CRA, and KH designed the study. CC carried out the experiments and wrote the original draft. GR performed sediment characterization. KH, AML, and CRA wrote, reviewed, and edited the manuscript. All authors discussed the results and commented on the manuscript.

**Funding** This work was supported by the Institut Universitaire de France (IUF) and MITI-CNRS (Métallo-Mix).

**Data availability** The study's data are available on request.

## Declarations

**Ethics approval** The authors mentioned in the manuscript have agreed for authorship, read and approved the manuscript, and gave consent for submission and subsequent publication of the manuscript.

**Consent to participate** All authors have consented the manuscript content for publication.

**Consent for publication** The paper is submitted with the consent of all listed authors.

**Competing interests** The authors declare no competing interests.

## References

- Agunbiade FO, Moodley B (2016) Occurrence and distribution pattern of acidic pharmaceuticals in surface water, wastewater, and sediment of the Msunduzi River, Kwazulu-Natal, South Africa. *Environmental Toxicology and Chemistry* 35:36–46
- Alexy R, Kumpel T, Kümmerer K (2004) Assessment of degradation of 18 antibiotics in the closed bottle test. *Chemosphere* 57:505–512
- Banzhaf S, Nödler K, Licha T, Krein A, Scheytt T (2012) Redox-sensitivity and mobility of selected pharmaceutical compounds in a low flow column experiment. *Science of the total environment* 438:113–121
- Bowman R (1984) Evaluation of some new tracers for soil water studies. *Soil Science Society of America Journal* 48:987–993
- Boxall A (2008) Fate of veterinary medicines applied to soils, Pharmaceuticals in the environment. Springer, pp. 103–119
- Champagne C, Gardner N, Brochu E, Beaulieu Y (1991) The freeze-drying of lactic acid bacterial. A review. *Canadian Institute of Food Science and Technology Journal* 24:118–128
- Chang B-V, Ren Y-L (2015) Biodegradation of three tetracyclines in river sediment. *Ecological Engineering* 75:272–277
- Conde-Cid M, Núñez-Delgado A, Fernández-Sanjurjo MJ, Álvarez-Rodríguez E, Fernández-Calviño D, Arias-Estévez M (2020) Tetracycline and sulfonamide antibiotics in soils: presence, fate and environmental risks. *Processes* 8:1479
- DeVries SL, Zhang P (2016) Antibiotics and the terrestrial nitrogen cycle: a review. *Current Pollution Reports* 2:51–67
- Dinh QT, Moreau-Guigon E, Labadie P, Alliot F, Teil M-J, Blanchard M, Chevreuril M (2017) Occurrence of antibiotics in rural catchments. *Chemosphere* 168:483–490
- Fan N-S, Bai Y-H, Chen Q-Q, Shen Y-Y, Huang B-C, Jin R-C (2020) Deciphering the toxic effects of antibiotics on denitrification: process performance, microbial community and antibiotic resistance genes. *Journal of environmental management* 262:110375
- Galloway JN, Dentener FJ, Capone DG, Boyer EW, Howarth RW, Seitzinger SP, Asner GP, Cleveland CC, Green P, Holland EA (2004) Nitrogen cycles: past, present, and future. *Biogeochemistry* 70:153–226



- Ghosh S, Sadowsky M, Roberts M, Gralnick J, LaPara T (2009) Sphingobacterium sp. strain PM2-P1-29 harbours a functional tet (X) gene encoding for the degradation of tetracycline. *Journal of applied microbiology* 106:1336–1342
- Gibs J, Heckathorn HA, Meyer MT, Klapinski FR, Alebus M, Lippincott RL (2013) Occurrence and partitioning of antibiotic compounds found in the water column and bottom sediments from a stream receiving two wastewater treatment plant effluents in Northern New Jersey, 2008. *Science of the total environment* 458:107–116
- Girardi C, Greve J, Lamshöft M, Fetzer I, Miltner A, Schäffer A, Kätner M (2011) Biodegradation of ciprofloxacin in water and soil and its effects on the microbial communities. *Journal of hazardous materials* 198:22–30
- Harrower J, McNaughtan M, Hunter C, Hough R, Zhang Z, Helwig K (2021) Chemical fate and partitioning behavior of antibiotics in the aquatic environment—a review. *Environmental toxicology and chemistry* 40:3275–3298
- Jia D, Li Q, Hanna K, Mailhot G, Brigante M (2021) Efficient removal of estrogenic compounds in water by MnIII-activated peroxymonosulfate: mechanisms and application in sewage treatment plant water. *Environmental Pollution* 288:117728
- Kühne M, Ihnen D, Möller G, Agthe O (2000) Stability of tetracycline in water and liquid manure. *Journal of Veterinary Medicine Series A* 47:379–384
- Kümmerer K (2008) Pharmaceuticals in the environment—a brief summary, Pharmaceuticals in the Environment. Springer, pp. 3–21
- Laverman AM, Van Cappellen P, van Rotterdam-Los D, Pallud C, Abell J (2006) Potential rates and pathways of microbial nitrate reduction in coastal sediments. *FEMS microbiology ecology* 58:179–192
- Liu C, Xu J, Lee D-J, Yu D, Liu L (2016) Denitrifying sulfide removal process on high-tetracycline wastewater. *Bioresource technology* 205:254–257
- Loftin KA, Adams CD, Meyer MT, Surampalli R (2008) Effects of ionic strength, temperature, and pH on degradation of selected antibiotics. *Journal of environmental quality* 37:378–386
- Luo Y, Xu L, Rysz M, Wang Y, Zhang H, Alvarez PJ (2011) Occurrence and transport of tetracycline, sulfonamide, quinolone, and macrolide antibiotics in the Haihe River Basin, China. *Environmental science & technology* 45:1827–1833
- Martin SB, Shchukarev A, Hanna K, Boily J-F (2015) Kinetics and mechanisms of ciprofloxacin oxidation on hematite surfaces. *Environmental science & technology* 49:12197–12205
- Nowara A, Burhenne J, Spieller M (1997) Binding of fluoroquinolone carboxylic acid derivatives to clay minerals. *Journal of Agricultural and Food Chemistry* 45:1459–1463
- Pallud C, Meile C, Laverman A, Abell J, Van Cappellen P (2007) The use of flow-through sediment reactors in biogeochemical kinetics: methodology and examples of applications. *Marine Chemistry* 106:256–271
- Pan L-j, Li J, Li C-x, Yu G-w, Wang Y (2018) Study of ciprofloxacin biodegradation by a *Thermus* sp. isolated from pharmaceutical sludge. *Journal of hazardous materials* 343:59–67
- Pan M, Chu L (2016) Adsorption and degradation of five selected antibiotics in agricultural soil. *Science of the Total Environment* 545:48–56
- Pavlović DM, Čurković L, Grčić I, Šimić I, Župan J (2017) Isotherm, kinetic, and thermodynamic study of ciprofloxacin sorption on sediments. *Environmental Science and Pollution Research* 24:10091–10106
- Payne W (1973) Reduction of nitrogenous oxides by microorganisms. *Bacteriological reviews* 37:409–452
- Rabølle M, Spliid NH (2000) Sorption and mobility of metronidazole, olaquinox, oxytetracycline and tylosin in soil. *Chemosphere* 40:715–722
- Roose-Amsaleg C, Yan C, Hoang A-M, Laverman AM (2013) Chronic exposure of river sediments to environmentally relevant levels of tetracycline affects bacterial communities but not denitrification rates. *Ecotoxicology* 22:1467–1478
- Rusch M, Spielmeier A, Zorn H, Hamscher G (2019) Degradation and transformation of fluoroquinolones by microorganisms with special emphasis on ciprofloxacin. *Applied microbiology and biotechnology* 103:6933–6948
- Sarmah AK, Meyer MT, Boxall AB (2006) A global perspective on the use, sales, exposure pathways, occurrence, fate and effects of veterinary antibiotics (VAs) in the environment. *Chemosphere* 65:725–759
- Shackelford CD, Daniel DE (1991) Diffusion in saturated soil. I: Background. *Journal of Geotechnical Engineering* 117:467–484
- Shan J, Yang P, Rahman MM, Shang X, Yan X (2018) Tetracycline and sulfamethazine alter dissimilatory nitrate reduction processes and increase N<sub>2</sub>O release in rice fields. *Environmental Pollution* 242:788–796
- Shao S, Wu X (2020) Microbial degradation of tetracycline in the aquatic environment: a review. *Critical reviews in biotechnology* 40:1010–1018
- Sithole B, Guy R (1987) Models for tetracycline in aquatic environments. *Water, Air, and Soil Pollution* 32:303–314
- Thuy HTT, Loan TTC (2014) Degradation of selected pharmaceuticals in coastal wetland water and sediments. *Water, Air, & Soil Pollution* 225:1–9
- Tolls J (2001) Sorption of veterinary pharmaceuticals in soils: a review. *Environmental science & technology* 35:3397–3406
- Ure A, Quevauviller P, Muntau H, Griepink B (1993) Speciation of heavy metals in soils and sediments. An account of the improvement and harmonization of extraction techniques undertaken under the auspices of the BCR of the Commission of the European Communities. *International journal of environmental analytical chemistry* 51:135–151
- Vasudevan D, Bruland GL, Torrance BS, Upchurch VG, MacKay AA (2009) pH-dependent ciprofloxacin sorption to soils: interaction mechanisms and soil factors influencing sorption. *Geoderma* 151:68–76
- Vree T, Wijnands W, Guelen P, Baars A, Hekster Y (1986) Pharmacokinetics: metabolism and renal excretion of quinolones in man. *Pharmaceutisch Weekblad* 8:29–34
- Wang H, Yao H, Sun P, Li D, Huang C-H (2016) Transformation of tetracycline antibiotics and Fe (II) and Fe (III) species induced by their complexation. *Environmental science & technology* 50:145–153
- Wang Q, Li X, Yang Q, Chen Y, Du B (2019) Evolution of microbial community and drug resistance during enrichment of tetracycline-degrading bacteria. *Ecotoxicology and environmental safety* 171:746–752
- Willingham TW, Werth CJ, Valocchi AJ, Krapac IG, Toupiol C, Stark TD, Daniel DE (2004) Evaluation of multidimensional transport through a field-scale compacted soil liner. *Journal of geotechnical and geoenvironmental engineering* 130:887–895
- Xu L, Zhang H, Xiong P, Zhu Q, Liao C, Jiang G (2021) Occurrence, fate, and risk assessment of typical tetracycline antibiotics in the aquatic environment: a review. *Science of the Total Environment* 753:141975
- Xu X-R, Li X-Y (2010) Sorption and desorption of antibiotic tetracycline on marine sediments. *Chemosphere* 78:430–436
- Yan C, Dinh QT, Chevreuil M, Garnier J, Roose-Amsaleg C, Labadie P, Laverman AM (2013) The effect of environmental and therapeutic concentrations of antibiotics on nitrate reduction rates in river sediment. *Water Research* 47:3654–3662
- Yang J-F, Ying G-G, Zhao J-L, Tao R, Su H-C, Chen F (2010) Simultaneous determination of four classes of antibiotics in sediments of the Pearl Rivers using RRLC–MS/MS. *Science of the Total Environment* 408:3424–3432

- Yi K, Wang D, Li X, Chen H, Sun J, An H, Wang L, Deng Y, Liu J, Zeng G (2017) Effect of ciprofloxacin on biological nitrogen and phosphorus removal from wastewater. *Science of the Total Environment* 605:368–375
- Yuan S, Wang Z, Wang Y, Yang H, Song Y, Bu N, Wang L, Zhang L (2021) Nitrogen removal, sludge activity and bacterial community in a sequencing batch reactor at different ciprofloxacin and ibuprofen concentrations. *Environmental Technology & Innovation* 24:101814
- Zhang C-L, Guo X-L, Li B-Y, Wang Y (2012) Biodegradation of ciprofloxacin in soil. *Journal of Molecular Liquids* 173:184–186
- Zhang G, Liu X, Sun K, Zhao Y, Lin C (2010) Sorption of tetracycline to sediments and soils: assessing the roles of pH, the presence of cadmium and properties of sediments and soils. *Frontiers of Environmental Science & Engineering in China* 4:421–429
- Zhang H, Huang C-H (2005) Oxidative transformation of fluoroquinolone antibacterial agents and structurally related amines by manganese oxide. *Environmental Science & Technology* 39:4474–4483
- Zhang X, Han H, Zheng X, Yu T, Chen Y (2019) Tetracycline-induced effects on the nitrogen transformations in sediments: roles of adsorption behavior and bacterial activity. *Science of the Total Environment* 695:133811
- Zhao Y, Gu X, Gao S, Geng J, Wang X (2012) Adsorption of tetracycline (TC) onto montmorillonite: cations and humic acid effects. *Geoderma* 183:12–18
- Zhou L-J, Ying G-G, Zhao J-L, Yang J-F, Wang L, Yang B, Liu S (2011) Trends in the occurrence of human and veterinary antibiotics in the sediments of the Yellow River, Hai River and Liao River in northern China. *Environmental Pollution* 159:1877–1885
- Zhou L, Martin S, Cheng W, Lassabatere L, Boily J-F, Hanna K (2019) Water flow variability affects adsorption and oxidation of ciprofloxacin onto hematite. *Environmental science & technology* 53:10102–10109
- Zhu D, Hyun S, Pignatello JJ, Lee LS (2004) Evidence for  $\pi$ - $\pi$  electron donor-acceptor interactions between  $\pi$ -donor aromatic compounds and  $\pi$ -acceptor sites in soil organic matter through pH effects on sorption. *Environmental Science & Technology* 38:4361–4368

**Publisher's note** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Springer Nature or its licensor holds exclusive rights to this article under a publishing agreement with the author(s) or other rightsholder(s); author self-archiving of the accepted manuscript version of this article is solely governed by the terms of such publishing agreement and applicable law.