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Original Article

Role of organic matter, clay, and iron contents in the sorption of oxytetracycline on river sediments

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Abstract

Background: Oxytetracycline (OTC) is a widely-used antibiotic; metabolism studies indicate only partial assimilation of it inside the body. Traditional wastewater treatment plants cannot remove OTC, and this results in the release of considerable amounts of the drug into aquatic environments. There is much concern over the role of residual antibiotics in the development of new generations of bacteria with modified resistance to the antibiotics. The present work investigated the possibility of OTC sorption on river sediments.

Methods: Seven sediment samples were collected from various locations and depths of the Passaic River in New Jersey. The texture, clay, extractable iron, and organic matter contents of the sediments were determined. Pyrolysis-gas chromatography-mass spectrometric (Py GC-MS) analysis indicated the presence of 3 categories of organic materials: petroleum hydrocarbons, anthropogenic, and plant residual materials. The sediment samples were equilibrated with OTC solutions for 24 hours followed by centrifugation and syringe filtration. The residual OTC contents were determined by high performance liquid chromatography.

Results: It appeared that 35%-60% fractions of OTC were retained by the sediments. The sorption capacity values of the sediments were correlated with clay content, organic matter content, and available iron. A poor correlation was found between adsorption capacity and clay content in the presence of organic matter and iron. Meanwhile, a relatively strong correlation was found between adsorption capacity with the iron, $R^2 = 0.7499$, and organic matter contents of the sediments, $R^2 = 0.7899$. Thus, the sorption of OTC on sediments is governed by all constituents.

Conclusion: It was concluded that the antibiotic-sediment interaction is controlled mainly by the organic matter and iron contents.

Keywords: Oxytetracycline, sorption, Passaic River sediment, Organic matter, Pyrolysis gas chromatography-mass spectrometry, Py GC-MS

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Introduction

The production and use of drugs are increasing worldwide. Antibiotics are among the most common medications used for human and veterinary treatments. As a result, when sewage sludge and manure are used as fertilizers on agricultural land, they are often contaminated with antibiotics (1). The fate of drugs and drug metabolites in the environment is of increasing concern around the globe. Studies have shown that a large percentage of consumed antibiotics is excreted without change (2) into the hydrosphere. Many researchers have detected various antibiotics in water samples (3). Sewage treatment plants do not remove residual antibiotics from wastewater (4), and this contributes to the risk of new generations of bacteria with modified resistance to antibiotics being created (5,6). The fate of pharmaceuticals in the environment is not different from that of other organic chemicals such as pesticides (7). Antibiotics appear in the environment when sewage sludge, manure, and other organic additives are applied to soils. Residual antibiotics have been detected in soils in varying concentrations (8,9). Oxytetracycline (OTC) is among the most frequently existing antibiotics in river sediments. A level of 0.52-2.68 ng g⁻¹ of OTC was found in Yangtze Estuary sediments (10). The highest antibiotic concentration, 4695 ng g⁻¹ of OTC was found in estuarine sediment from Ziya New River (11).

Efforts worldwide are directed towards establishing methods to remove TC from water using various sorbents such as activated charcoals and clay minerals (12,13). Clay minerals, like montmorillonite, are effective at removing them from water (14). The use of clay in sorption studies has provided useful insights into the fate of antibiotics in river sediment systems. Knowledge of persistence pollutants and their sorption behavior is crucial for the evaluation of the mobility (7). Bezza et al (15) investigated the significance of pH, organic matter, and the presence

of metal ions on the extent of adsorption of TC. The role and function of natural organic material in both aquatic and terrestrial environments is strongly related to nutrient availability for plants. It can also influence the physico-chemical conditions of soil and sediments as well as their buffering and exchange capacities. These are relevant for the immobilization and mobilization of many environmental pollutants (16). Shareef and Ahmed (17) found that OTC strongly and preferentially adsorbs on the surface of local Iraqi soils through a bonding mechanism. Kasteel et al (18) reported that the sorption of antibiotics into soil was time-dependent and affected by pH with a higher sorption capacity for loamy sand. Li and Zhang (19) studied the effects of organic carbon (OC) content and particle size on the adsorption capacity of OTC on 2 marine sediments. They studied the kinetics and proved that diffusive mass transfer was the dominant mechanism of time-dependent adsorption of OTC; they also reported that its release from marine sediment was mildly hysteretic. For some antibiotics, like chlortetracycline, the sorption to sandy loam and clay is rapid; more than 95% of it is adsorbed within 10 minutes of contact. A comparable proportion of tylosin is adsorbed within 3 hours (20).

During their study of OTC sorption on organic materials, MacKay and Canterbury (21) found that there was no detectable sorption on cellulose or lignin sorbents containing few metal-complexing ligand groups. The sorption to humic acid increased with Fe(III)-amended clean humic acid with K(d) values of 250 000 L kg^{-1}. They suggested the formation of ternary complexes with humic acid (organic matter), metals, and pharmaceutical ligand groups. This reflects the importance of organic matter as a sorbent phase in soils and sediments for pharmaceutical compounds. Jones et al (22) reported that the interaction of OTC with soil organic matter, clay minerals, and metal oxides accounts for the strong sorption of the antibiotic. Soil texture, iron oxide content, and cation exchange capacity (CEC) have the greatest influence on the extent of OTC sorption in soils with OC (22).

Recently, Kong et al (23) proved that, in addition to the permanent CEC, soils with relatively high illite content have a high OTC sorption capacity. However, the availability of sorbed OTC increases as indicated by the release of the sorbed OTC from soils into a slightly alkaline magnesium chloride solution. Their findings indicated that soil organic matter and clay are effective in the sorption of OTC and its potential availability. Jia et al (24) showed that the sorption of OTC on biochar depends highly on the pH of the solution. Their results also indicated the enhancement of sorption by the presence of Cu^{2+} ions. Conversely, the sorption of OTC showed a slight reduction when Pb^{2+} was present in acidic conditions.

In the present work, selected Passaic River sediment samples were used for the removal of OTC from water. The sorption capacity of such riverine sediments was correlated with the clay content, iron, and organic matter contents.

Materials and Methods
Apparatus
Pyrolysis GC-MS
All sediment samples were dried and milligram quantities were placed in the pyrolytic cell together with 5 µL of a solution containing D-naphthalene, D-anthracene, and D-pyrene (Sigma Aldrich and Cambridge Isotope Laboratories). The spike concentration was manipulated such that each injection introduced 24.50 ng of D-naphthalene and 27.00 ng of D-anthracene into the chromatographic system. D-pyrene was not used for quantization. A CDS model 1500 pyrolizer system was used to heat both the sediment and phragmites samples to 610°C for 20 seconds under a helium atmosphere. The GC column used for sediment analysis was 0.25 mm ID, 60 m in length, and packed with the dimethyl polysiloxane stationary phase (Restek catalog number 13326, Restek Chromatography, Bellefonte, PA) The GC column used for the phragmites analysis was an Agilent (J&W) 30 m, DB1-MS, 0.25 mm ID, (Agilent, catalog number 122-0132UI). The details of the GC temperature programs were described in detail elsewhere (25). Operating in full-scan mode, the mass spectrometer was set to 50-550 Da, 1.08 scans/s, and 70 eV ionization voltage. Peak identification was based on a combination of molecular weight and retention time window for each compound.

HPLC analysis
OTC concentrations were analyzed by high performance liquid chromatography (HPLC). The conditions and details of the analysis system are described elsewhere (14).

Induced coupled plasma analysis
The sediments (0.50 g) were extracted with 10 mL of 0.5 M HCl for 2 hours in 50-mL centrifuge plastic tubes. The tube contents were centrifuged and filtered with a 0.2-µ syringe microfilter. The filtrate was analyzed for iron using induced coupled plasma (ICP) optical emission spectrometry on an ICP-MS Thermo X-Series II, Thermo-Electron, San Hose, CT). The analysis was done in duplicate. The standard conditions recommended by the manufacturer were used. The results are given in Table 1.

Materials and reagents
OTC, C$_{22}$H$_{24}$N$_2$O$_9$, and HPLC solvents used in this study were as described earlier (14). NanoPure water was used for the preparation and dilution of working solutions. Buffer solutions were prepared from Pipes, which is the common name for piperazine-N, N′-bis(2-ethanesulfonic acid) as described earlier (14).

Sediments
Seven sediment samples were used in this study, comprising 4 locations (5A, 7A, 9A, and 10A) and three different depths (26). Figure 1 shows a satellite image of the NY/NJ harbor estuary system with core locations.

Table 1. The clay, organic (LOI%) and extractable iron contents of the selected sediment samples

Soil Code	Depth, cm	Clay content	Organic content, LOI, %	Iron, %
5A S38	330-340	26.18	4.59	0.55
5A S46	449-469.5	3.15	4.02	0.235
7A S34	435-450	28.26	7.613	0.721
9A S06	45-54	7.29	8.49	0.601
9A S34	547-566	19.72	16.63	0.735
10A S28	203-212	20.93	13.03	0.666
10A S46	365-375	12.25	2.82	0.36

Figure 1. Satellite image of the NY/NJ harbor estuary system with core locations.

Procedures

Sorption

The sorption of OTC was carried out in 15-mL centrifuge tubes in the presence of two levels of sediment samples: 0.25 g and 0.5 g. The procedures followed were previously fully described by Barbooti et al (14).

Organic matter content was determined using the loss-on-ignition (LOI) standard test in which the sample was weighed on an analytical balance before and after heating overnight at 400°C. This temperature was recommended by the USEPA to prevent the destruction of carbonates and a resulting positive error (27).

Removal of organic matter

The organic matter of the sediments was removed by adding the sediment sample (2.5 g) into 50 mL of sodium hypochlorite solution at pH 12 (28) with occasional swirling. Alternatively, 2.5 g sediments were treated with several volumes of hydrogen peroxide (29) and kept overnight with occasional swirling until the gas evolution ceased.

The materials were then washed several times with deionized water to remove any residual salt or excess oxidant.

Petroleum hydrocarbon determination

A sediment sample (1-5 g) was equilibrated with 10 mL of the solvent for 4 minutes and left to stand for one minute. The solution was decanted through a 0.2 μ filter into a glass cell containing developer material at a ratio of 2:3 (hydrocarbon solution: developer solution), mixed for 20 seconds, and left to stand for 10 minutes. The resultant emulsion was quantitated by turbidimetry (30).

Results

Table 1 shows the clay contents, organic matter (measured as LOI%), and extractable iron contents for the selected sediment samples. The clay contents of the sediments ranged 12%-28%, except for sample 5A S46 which had a relatively low clay content of 3.15%. The LOI measurements indicated that the sediments were relatively rich with organic materials (4%-16%) with the exception of sample 10A S46 which had the lowest LOI% of 2.82%. All sediment samples had an appreciable extractable iron content (0.23%-0.72%).

The sediment samples were pyrolyzed at 600°C and the products were analyzed by GC. Some of the GC-pyrograms are shown in Figure 2. The signals related to plant materials resembled those given by reed powder sampled from Montclair, NJ (Figure 3). The characterization of
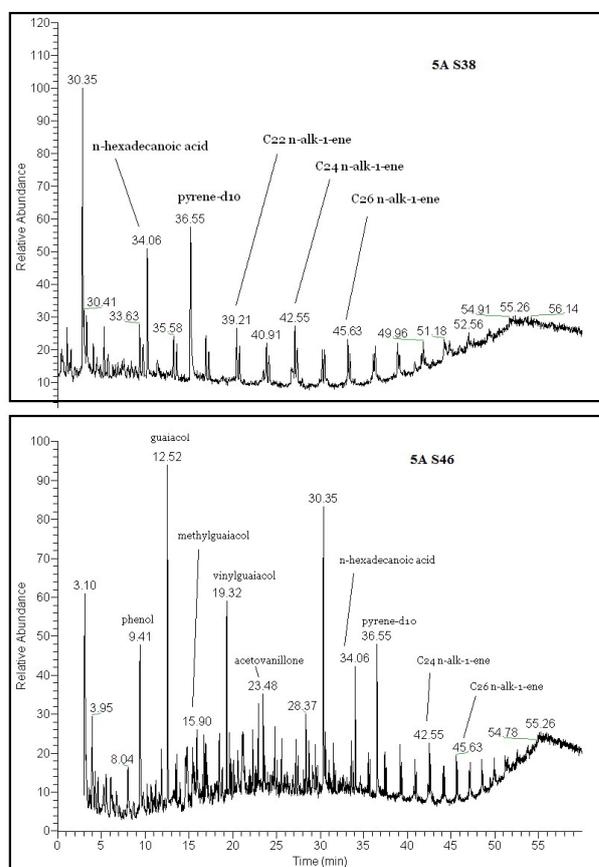
Figure 2. Py GC-MS of sediments 5A S38 and 5A S46.

Table 2. Py GC-MS characterization of sediments organic matter, ng.mg^{-1}

Group compound	Sediment						
	5A38	5A 46	7A34	9A06	9A34	10A 28	10A46
Total fatty acids	9.49	0.23	0.56	1.29	1.87	3.46	0.24
Total angiosperm lignin markers	0	7.26	1.07	9.06	2.51	0	0
Total lignin markers	92.99	24.54	7.54	30.12	61.94	1.32	1.32
Total petroleum markers	0	0	2.34	1.96	7.43	0.4	0.4
Total polysaccharide markers	119.92	6.69	4.63	18.01	19.02	1.83	1.83
Total sewage markers	0	0.03	0.24	0.12	3.1	0.16	0.16
Total sulfur compounds	46.47	0.23	5.01	2.4	7.78	1.19	1.19

each group was indicated by some marker compounds as given in Table 2. Figure 4 shows the pyrograms of one of the sediments after treatment with hydrogen peroxide displayed with that of the untreated sediments for comparison.

The extent of OTC sorption on the sediment samples for two levels of solid sorbent to water is indicated in Table 3. It appears that the extent of adsorption did not double when the soil contents in water were doubled. To account for the extent of OTC sorption on the Passaic sediments, the results were correlated with the various components. Clay materials were among the successful sorbents of the antibiotic, and hence, the correlation began with the clay contents of the sediments. A plot of the extent of OTC sorption against the clay contents of the soils under investigation is shown in Figure 5. The correlation coefficient (R^2) was 0.318 for 2.5 g soil /L and 0.3036 for 5.0 g soil/L; the intercept was 32.7.

The sorption efficiency of the sediment samples was correlated with the available iron content (Table 1), and the plot is shown in Figure 6. The sorption data were correlated with the LOI percentages as shown in Figure 7, and a linear plot with a correlation coefficient (R^2) of 0.7499 could be obtained, which indicates a direct relationship between OTC adsorption and organic matter content.

Discussion

Organic Matter Characterization

Sediment samples were analyzed with pyrolysis GC-Ms to identify and quantify organic compounds. Three categories of organic materials were identified in the pyrolyzed samples: petroleum hydrocarbons, anthropogenic materials, and plant residual materials (26). The chosen soil samples were characterized by biomass origin and hydrocarbon organic matter, which increases in the order of
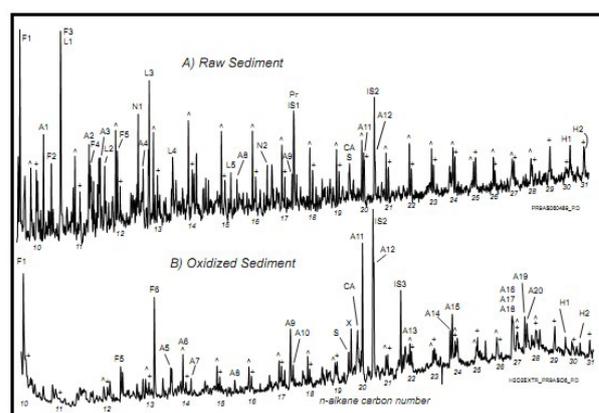
Figure 4. Py-GC of sediment 9A (45-54 cm core depth): (A) before and (B) after oxidation with hydrogen peroxide.

5A< 7A< 9A<10A of the cores used in this study (31). The pyrogram of the sediments treated by hypochlorite exhibited only the base line and therefore indicated the complete removal of all types of organic matter. The H$_2$O$_2$ treatment resulted in the complete disappearance of the plant residues peaks (Figure 4). Meanwhile, the hydrogen peroxide treatment gave only a slight reduction in the peaks of petroleum hydrocarbons.

The plot of correlation of the adsorption capacity with the clay content of sediments (Figure 5) indicated only weak correlations for the clay contents in the suspension. Also, the intercept = 32.7, indicative of the activity of other parameters on sorption and that clay is not the only factor in the determination of adsorption capacity. Thus, sediment parameters other than clay content are predominant in this respect. Comparable results were obtained by Thiele-Bruhn (1), who reported a correlation coefficient of 0.34 with the clay content of soil. Kasteel et al (18) reported

Table 3. The sorption of oxytetracycline in soil samples

Soil code	% Sorbed antibiotic		Cs, mmol/g	Cs, mmol/g
	2.5 g Soil/L	5.0 g Soil/L	5 g	2.5
5A S38	38.1/30.9	50.2/ 20.1	0.0402	0.1173
5A S46	30.2/24	39.8/16	0.0318	0.07682
7A S34	47.0/37	52.6/21	0.0421	0.13305
9A S06	43.9/35	53.5/22	0.0428	0.4815
9A S34	52.2/41	60.9/24	0.0487	0.213
10A S28	59.5/48	67.9/27	0.0543	0.2274
10A S46	30.1/24	38.8/15	0.0310	0.1959
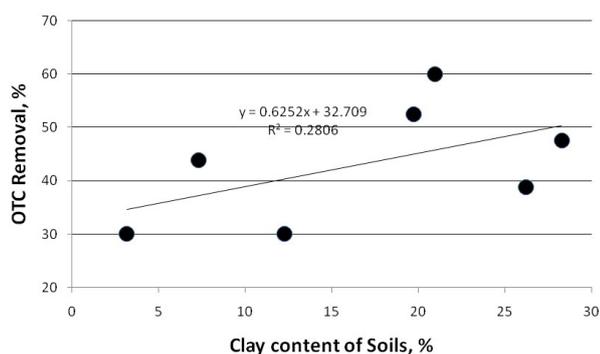
Figure 5. Correlation of adsorption capacity with clay content of Passaic sediments at 2 g/L level.

Figure 6. Effect of available iron content of sediments on sorption efficiency for 2.5 g/L and 5 g/L levels.

Figure 7. Dependence of adsorption capacity on the organic matter of soil (Loss on Ignition) for 5 g/L.

that the sorption of antibiotics into soil was affected by the equilibration time and pH of the solution. A higher sorption capacity was reported for loamy sand.

The plot of the sorption capacity against the iron content of the sediments (Figure 6) showed a reasonable correlation with R^2 values of 0.7499 and 0.7074 for 2.5 and 5.0 g/L sediment samples, respectively. Thus, the sorption efficiency is linearly changing with the available iron content. The effect of organic matter on adsorption is shown in Figure 7. The relatively high R^2 of 0.7899 indicated a direct relationship of the OTC adsorption with the organic matter content of the soil samples studied. Pateiro-Moure et al (32) reported that the universal soil colloid that binds most herbicides is organic matter; however, metallic hydrous oxides might also have some influence. Soil texture, CEC, and iron oxide content seemed to have some influence on the extent of TC sorption in soils with an OC content between 0% and 4% (22). Residual concentrations of pharmaceutical antibiotics exert a temporary selective pressure on soil microorganisms, which is clearly influenced by soil adsorption (1).

Thus, the entire adsorption is associated with the organic compounds available in Passaic River sediments.

Natural organic matter in soils interacts with surfaces of inorganic materials, primarily aluminosilicates or clay minerals, to form a strongly associated organo-mineral composite known as humin. Upon removal of the organic matter from the soils, surface area increased and surface pore size decreased (33). This may account for the slight change in the sorption properties of the Passaic sediments after the organic matter was removed.

MacKay and Canterbury (21) referred the enhanced sorption of OTC into soils rich with organic matter to the formation of complexes. This applies to the soil samples in this study where low clay content samples showed considerable OTC sorption due to the occurrence of organic matter.

Antibiotics may appear in the environment when manure, sewage sludge, or other organic amendments are added to soils. The sorption of chlortetracycline (CTC) and tylosin in sandy loam and clay occurs very fast. More than 95% of the CTC adsorption is completed within 10 minutes on both soils and of TYL within 3 hours (20). When they
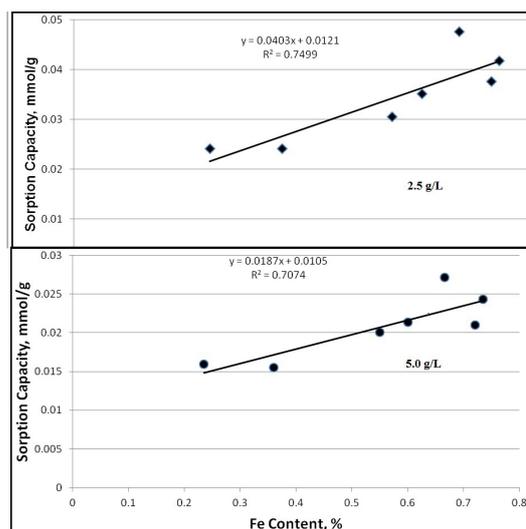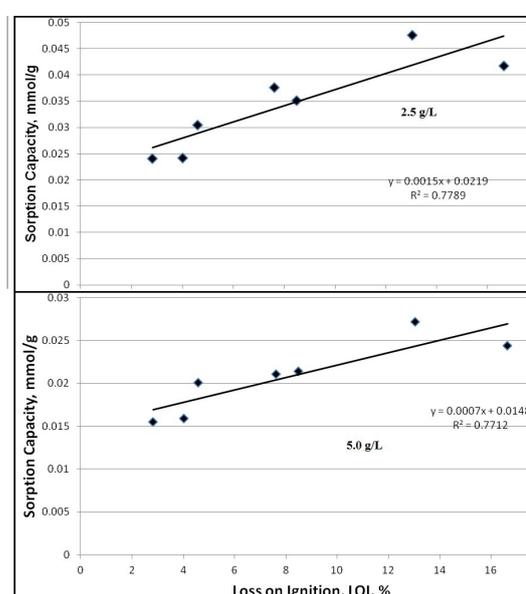
interpreted the sorption of OTC onto marine sediments, Pouliquen and Le Bris (34) concluded that sorption increased with sediment content in mineral and organic matter and in particles of less than 63 μm in diameter.

Conclusion

Pyrolysis GC-MS and spectrophotometric measurements may be used to investigate the role of organic matter and iron in the interaction of OTC with river sediments. The organic matter of sediments has petroleum, plant, and anthropological origins. Non-petroleum organic matter is effective and has a direct relationship with the sorption capacity of the sediments. To a lesser extent, iron content is effective in determining sediment sorption capacity. Although clay materials are active sorbents for OTC, the presence of organic matter reduces such activity.

Ethical issues
The author hereby certifies that all data collected during the study is as stated in the manuscript, and no data from the study has been or will be published separately elsewhere.

Competing interests
The author declares that he has no competing interests.

Author's contribution
MMB is the single author of the paper.

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