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Simultaneous extraction and analysis of 11 tetracycline and sulfonamide antibiotics in influent and effluent domestic wastewater by solid-phase extraction and liquid chromatography-electrospray ionization tandem mass spectrometry

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Abstract

Wastewater treatment plants (WWTPs) in which antibiotic compounds are not totally eliminated are considered to be point sources of antibiotic contamination in surface and ground waters. Therefore, there is a need for sensitive and reliable analytical methods for measuring these compounds in WWTP water matrices. This paper describes a simultaneous method for the determination of six tetracyclines (TCs) (oxytetracycline (OTC), tetracycline (TC), demeclocycline (DMC), chlortetracycline (CTC), doxycycline (DXC), meclocycline (MCC)) and five sulfonamides (SAs) (sulfathiazole (STZ), sulfamethazine (SMT), sulfachloropyridazine (SCP), sulfamethoxazole (SMX) and sulfadimethoxine (SDM)) using solid-phase extraction followed by liquid chromatography-ion trap tandem mass spectrometry. The average recovery of 11 antibiotics for simultaneous extraction was 83.3 ± 12.6 and 89.8 ± 11.5% for six TCs, and 95.2 ± 11.4 and 97.7 ± 10.6% for five SAs in the influent and effluent water, respectively. Matrix effects were found to be significant when measuring TCs but not SAs. The accuracy and day-to-day variation of the method fell within an acceptable range of 15% absolute. Method detection limits in wastewater matrices were between 0.03 and 0.07 μg/L. For the investigated 11 antibiotic compounds TC, DMC, CTC, DXC, SMT, SMX and SDM were found in the influents with a concentration range of 0.05–1.09 μg/L. CTC, DXC and SMX were also detected in the effluents with a concentration range of 0.06–0.21 μg/L. These results were compared with those in WWTP effluents of Canada, Germany and Switzerland.

Keywords: Antibiotics; Tetracyclines; Sulfonamides; Wastewater; WWTPs

1. Introduction

Tetracyclines (TCs) and sulfonamides (SAs) are widely used antibiotics in today's human and veterinary medicine practice. TCs (e.g. oxytetracycline (OTC), tetracycline (TC), demeclocycline (DMC), chlortetracycline (CTC), doxycycline (DXC), meclocycline (MCC)) are broad-spectrum bacteriostatic agents active against Gram-positive and Gram-negative bacteria that act by inhibiting protein synthesis. Their basic structures consist of a hydronaphthacene backbone containing four fused rings (Fig. 1). The various analogues differ primarily by substitutions of the fifth, sixth or seventh position on the backbone (Fig. 1). SAs (e.g. sulfathiazole (STZ), sulfamethazine (SMT), sulfachloropyridazine (SCP), sulfamethoxazole (SMX) and sulfadimethoxine (SDM)) are N-substituted derivatives of the substance sulfanilamide and compete with *p*-aminobenzoic acid in enzymatic synthesis of dihydrofolic acid (Fig. 1). This leads to a decreased availability of the reduced folates that are essential in the synthesis of nucleic acids. TCs in human medicine are continuing to be useful in treating a broad range of infections, including malaria and SAs are routinely used to treat human infection such as bronchitis, urinary tract and ear infections [1]. These compounds have been widely used both for prevention and treatment of disease and as feed additives

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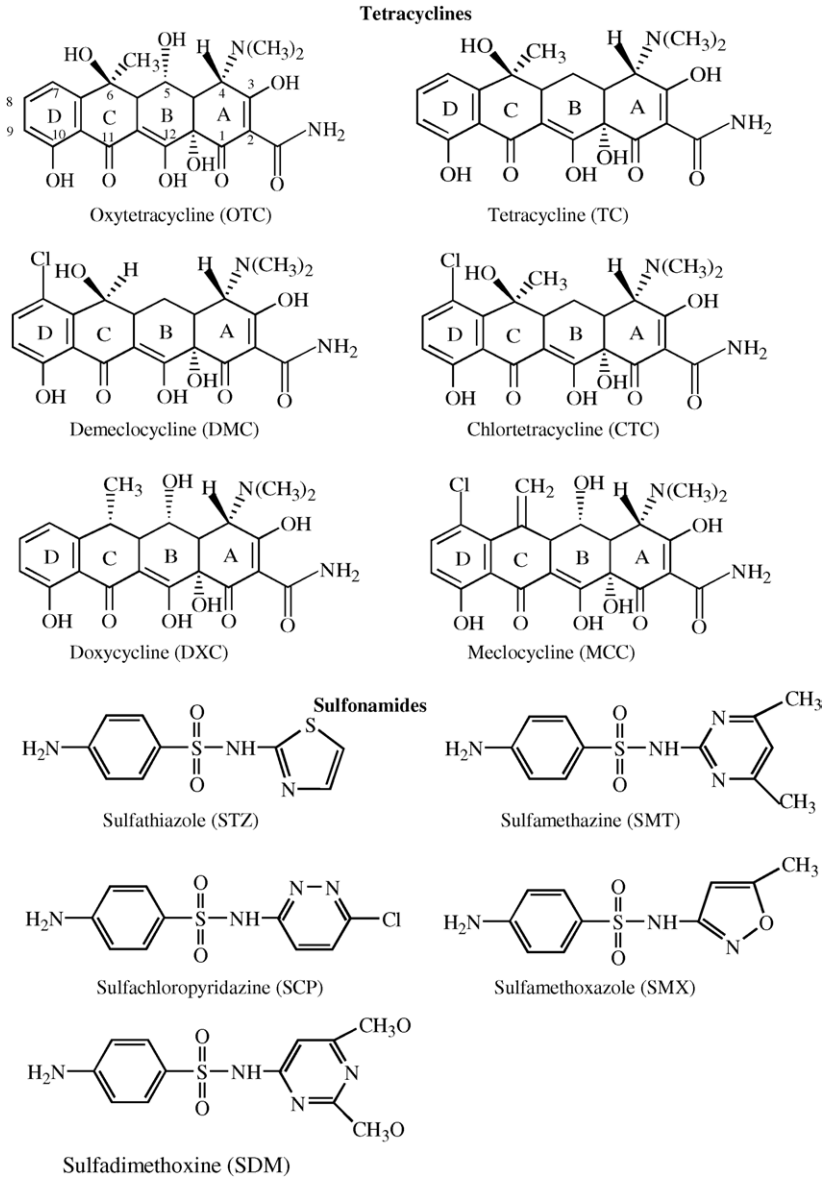

Fig. 1. Chemical structures of tetracyclines and sulfonamides.

to promote growth in animal feeding operations (AFOs) and concentrated animal feeding operations (CAFOs) [2].

A high percentage of antibiotics consumed by humans are ultimately excreted unchanged via urine and feces into domestic sewage, and are discharged to wastewater treatment plants (WWTPs). In WWTPs, these compounds are only partially eliminated and there is the potential for residues of antibiotics to be released in WWTP effluent into the aquatic environment. SMX has been found in WWTP effluents of Germany with a maximum concentration of 2.0 μg/L [3]. Miao et al. [4] measured maximum concentrations of 0.98 and 0.87 μg/L for TC and SMX in WWTP effluents of Canada. Researchers have shown that several classes of antibiotics (e.g. TCs and SAs) are present in hog waste lagoons at concentrations as high as 0.7 mg/L [5]. The U.S. Geological Survey reported that 95 organic wastewater contaminants containing antibiotics were found in 80% of the 139 streams sampled during 1999 and 2000 [6]. Antibiotic concentrations as high as 1.9 μg/L were found with the frequency (22%) of detection of at least one antibiotic in the 84–104 streams sampled and only 10 of 24 antibiotic compounds measured were not detected in any of the streams. Other studies by our research group have reported a substantial increase of TCs, SAs, macrolides and ionophore antibiotics along the flow path of the Cache La Poudre River in northern Colorado that is influenced by WWTP effluents and agricultural landscapes [7–9].

WWTPs are considered to be point sources of antibiotic contamination in surface and ground waters. Concerns have been raised regarding public health issues over the occurrence of antibiotics in the aquatic environment, and the potential exists for proliferation of resistant bacteria in