

Review

A review of occurrence of pharmaceuticals in sediments

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There is no doubt whatsoever that an increasing number of pharmaceuticals are being discharged in the aquatic environment. They may be present at trace levels. However, pharmaceuticals and their metabolites adverse effects on aquatic lives, animals and humans are a growing concern in the worldwide. Pharmaceuticals contamination of aquatic environment has been of major concern in recent years. Many studies have been published occurrence of pharmaceuticals in different parts of the world. Until now, there is little information about the occurrence of pharmaceuticals in sediment system. Therefore, in this review, focuses will be more on recent studies on the occurrence of detected pharmaceuticals in sediments.

Key words: Pharmaceuticals, sediment, aquatic environment.

INTRODUCTION

In modern society, an increasing number of pharmaceuticals and their residues are being discharged into the aquatic environment. These chemicals show a great difference in chemical composition, molecular weight and toxicity. There are many studies of occurrence of pharmaceuticals but, limited publications concern the occurrence of them in sediment. On the other hand, antibiotics and steroid hormones are reported in literature. However, it is not known how strongly the antibiotics are sorbed to sediments and under what circumstances they are bioavailable and active after sorption. All of them have been identified at low ng/kg level (Kummerer, 2009).

Silva et al. (2011) studied 43 pharmaceuticals in surface water, suspended solids and sediments in Ebro river in northeast of Spain. The 43 pharmaceuticals obtained belong to different therapeutic groups (analgesics and anti-inflammatory drugs, anti-ulcer agent, psychiatric drugs, antiepileptic drug, antibiotics, β -blockers, diuretics, lipid regulator and cholesterol lowering statin drugs, and anti-histamines). The highest concentrations were measured for acetaminophen (222

ng g⁻¹), mevastatin (99.4 ng g⁻¹) and tylosin A (71 ng g⁻¹). Other pharmaceuticals, such as erythromycin, ibuprofen and ranitidine were detected at maximum concentration of 33.5, 19.2 and 25.1 ng g⁻¹, respectively, while cimetidine and clofibrac acid were detected at levels below 20 ng g⁻¹. The other compounds were found at concentrations below 10 ng g⁻¹ in the sediments samples.

Savci (2013) studied ranitidine and showed that it is a drug responsible for disturbing the microbial ecology of surface waters. The study determined adsorption properties of ranitidine-live sludge system. In this way, kinetic and equilibrium biosorption data were obtained and the effect of several sludge dose (0.5 g and 1.0 g) in the biosorption process was evaluated.

Williams and Kookana (2010) investigated isotopic exchangeability as a measure of carbamazepine, an antiepileptic pharmaceutical compound, in river sediment. The sediment used for the batch sorption experiments was collected from Mackreath Creek, Scott Creek Conservation Park, South Australia. They used isotopic dilution technique for the sediments. They demonstrated the availability of a relatively quick and simple alternative

to batch desorption techniques for the assessment of the available fraction of organic compounds in sediments.

Although little is known about the environmental transport and fate of pharmaceuticals, many sorb the sediments; they are weak sorbates and it has been shown that they migrate through river bed sediments. Pharmaceuticals may present an exposure risk to aquatic organisms in waters and sediments, though toxicity levels are largely unknown. Sediment sorption is one of the mechanisms by which it is thought that pharmaceuticals may persist in the aquatic environment. It needs to be investigated.

Gong et al. (2011) investigated in 28 riverine sediments from the Pearl River system, China and analyzed them by an ultrasonication extraction and gas chromatography-mass spectrometry (GC-MS) method. The concentrations of 4-tert-octylphenol (OP), 4-nonylphenol (NP), and bisphenol A (BPA) in the sediments were in the ranges of <2.0 to 210, 107 to 16198 and <1.7 to 430 ng/g dw, respectively.

ESTROGENS IN SEDIMENTS

In the aquatic environment, exposure of organisms to an estrogenic substance has been linked to adverse endocrine effects such as feminization and imposex. Wang et al. (2011) investigated estrogenic compounds and estrogenic activity in the Liao River system using combined chemical analysis and *in vitro* bioassay. Selected target estrogenic compounds including 4-t-octylphenol (4-t-OP), 4-nonylphenols (4-NP), bisphenol-A (BPA), diethylstilbestrol (DES), estrone (E1), estradiol (E2), 17 α -ethinylestradiol (EE2), and triclosan (TCS) in the surfacewater and sediment were determined using GC-MS. Hájková et al. (2007) developed new GC-MS method for direct analysis of five major steroid estrogens (estrone, 17 β -estradiol, 17 α -ethinylestradiol, dienestrol and diethylstilbestrol) in river sediments. They used four GC-MS systems for analysis of underivatized analytes in purified extracts. They tried relatively low detection limits (1.5-5 ng g⁻¹ dried sediment). They achieved by use of a system combining low-pressure gas chromatography with a single-quadrupole mass analyzer (LP-GC-MS). Moreover, they emphasised that GCxGC-TOF-MS system enabled identification of several other non-target chemicals in purified sediment extracts.

ACIDIC PHARMACEUTICALS IN SEDIMENTS

Acidic pharmaceuticals are consumed in large quantities and were found in high concentrations in the aqueous environment. The parasiticide ivermectin was found in sediments close to fish farm (Davies et al., 1998). Varga et al., (2010) investigated selected acidic pharmaceuticals (ibuprofen, naproxen, ketoprofen, and diclofenac) in the Danube river water and sediment in Budapest (Hungary). These studies were carried out for one year. In sediments,

only naproxen and diclofenac were found in the range of 2 to 20 and 5 to 38 ng/g, respectively. They emphasized that the drug content of sediments depended on the drug concentration of aqueous phase and the Total organic carbon (TOC) content of the sediment.

Lei et al. (2009), studied level of six estrogens [diethylstilbestrol (DES), estrone (E1), β -estradiol (E2), estriol (E3), 17 α -ethinylestradiol (EE2) and β -estradiol 17-valerate (EV)] in water and sediment from three rivers in Tianjin area in China. They used gas chromatography-mass spectrometry (GC-MS). The concentrations of all six estrogens ranged from 0.98 to 51.6 ng g⁻¹ dry weight (dw) in sediments and varied for each river. Yamamoto et al. (2005), studied fate and partitioning of selected pharmaceuticals in aquatic environment. They selected two nonsteroidal anti-inflammatory drugs (NSAIDs), ibuprofen an acetaminophen and atenolol an antidepressant fluoxetine and their sorption coefficients on the basis of dissolved organic matter and model sediments were determined. Atenolol was resistant to biodegradation. Acetaminophen was only slightly bioaccumulative, ibuprofen was also highly biodegradable and fluoxetine had a relatively high bioaccumulation factor. Löffler et al. (2005) examined environmental fate of pharmaceuticals in water/sediment systems. They selected 10 pharmaceuticals and pharmaceuticals metabolites were investigated in water/sediment systems including both the analysis of water and sediment. The experiments covered the application of four 14C-labeled pharmaceuticals (diazepam, ibuprofen, iopromide, and paracetamol) for which radio-TLC analysis was used as well as six nonlabeled compounds (carbamazepine, clofibrac acid, 10,11-dihydro-10,11-dihydroxycarbamazepine, 2-hydroxyibuprofen, ivermectin, and oxazepam), which were analyzed via LC-tandem MS. Ibuprofen, 2-hydroxy-ibuprofen, and paracetamol displayed a low persistence with DT50 values in the water/sediment system. Jones et al. (2006), conducted to ascertain an understanding of the binding behavior of five drug substances (Ibuprofen, paracetamol, salbutamol, propranolol HCl, mefenamic acid) sorbing to the solid phase in a laboratory scale-activated sludge plant (Husmann unit). For comparison, uncontaminated river sediment was also used as a substrate.

All of the compounds tested partitioned more readily to the sludge than the sediment, likely because of the former's higher organic carbon content. Partitioning to the solid phase correlated roughly with predicted log Kow values.

ANTIBIOTICS IN SEDIMENTS

The environmental impacts of antibiotics in sediments have been studied by several authors. Yang et al. (2010) developed a simultaneous and analysis method for four classes of antibiotics sulfonamides (SAs), macrolides (MLs), fluoroquinolones (FQs) and tetracyclines (TCs) in sediment. Ofloxacin was found to have the highest con-

centration of 1560 µg/kg in sediment. The environmental fate of the antibiotics in the sediments is of great concern. Hu et al. (2012) investigated and identified 12 typical antibiotics in a typical river receiving sewage discharge. They measured the natural accumulation and attenuation of antibiotics in sediments. They established a method to prioritize the typical antibiotics in sediments. Zhou et al. (2011) indicated 17 commonly used anti-biotics (including fluoroquinolones, tetracycline, sulfo-namides, and macrolides) in the sediments of the Yellow River, Hai River and Liao River in northern China by using rapid resolution liquid chromatography-tandem mass spectrometry. Higher concentrations were detected for most antibiotics in the sediments of the Hai River than in the sediments of the other rivers. Norfloxacin, ofloxacin, ciprofloxacin and oxytetracycline in the three rivers were most frequently detected with concentrations up to 5770, 1290, 653 and 652 ng/g, respectively.

Terzic and Ahel (2011) developed a comprehensive analytical procedure for a reliable identification of nontarget polar contaminants in aquatic sediments. They used the application of ultra-high-pressure liquid chromatography (UHPLC) coupled to hybrid quadrupole time-of-flight mass spectrometry (QTOFMS). The procedure was applied for the analysis of freshwater sediment that was highly impacted by wastewater discharges from the pharmaceuticals industry. The major compounds included a series of polypropylene glycols ($n=3-16$), alkylbenzene sulfonate and benzalkonium surfactants as well as a number of various pharmaceuticals (chlorthalidone, warfarin, terbinafine, torsemide, zolpidem and macrolide antibiotics).

PERSPECTIVES

Human pharmaceutical products are great importance in the treatment of disease. However, they are designed to be biologically active. There are number of different ways these pharmaceutically active compounds get into the aquatic environment. One way is as a result of excretion following therapeutic use. A second way is through incorrect disposal methods. Hence, they become part of the waste water but, there are not necessarily removed when the waste water is passed through treatments plants (Zhou et al., 2009). This review highlights the fact of occurrences of the pharmaceuticals in river sediment.

Several of the pharmaceuticals detected are known to have detrimental impacts of concern, though little is yet known about their sedimentary concentrations of concern. The effects of many pharmaceuticals and their transportation products are not understood and require further study. Also, future research is needed to determine effects levels for pharmaceuticals. In addition to, future efforts are needed to understand routes of exposure and bioaccumulation pathways. There is need for efficient extraction methods suitable for sediments.

Biotransformation and sorption are considered impor-

tant for pharmaceuticals. Sorption has an important role in determining the fate of pharmaceuticals in the environment. Future studies are needed on both chemical structure of the metabolites, hydrolytic and photolytic products of pharmaceuticals and their antibacterial activity and persistence of transformation products.

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