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Occurrence of pharmaceutical compounds and pesticides in aquatic systems

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ABSTRACT

This paper deals with the detection and quantification of APIs and other priority substances in the Arade River estuary (Portugal) providing the usefulness of Polar Organic Compound Integrative Samplers (POCIS). Thirteen APIs were detected whose variation was site and time dependent. Caffeine was at the highest concentration (804 ± 209 ng/L) followed by theophylline (184 ± 44 ng/L). Other APIs were analgesic, anticonvulsant, non-steroidal anti-inflammatory drugs, anti-lipidemic, anxiolytic and antidepressants. Twenty pesticides comprising atrazine, diuron, isoproturon, terbutryn and simazine included in the Water Framework Directive priority list were also site and time dependent. Carbendazim occurred at the highest concentration (45 ± 18 ng/L at site 1) but atrazine, diuron, isoproturon and simazine levels were below the Environmental Quality Standards. Although the summer impact was unclear, the results highlighted POCIS suitability for profiling these contaminants. This is to our knowledge the first study concerning APIs and pesticides in this area.

1. Introduction

Pharmaceutical products have been used for centuries but, from an ecotoxicological viewpoint, active pharmaceutical ingredients (APIs) are considered emerging environmental contaminants since only recently there are suitable analytical and sampling techniques able to accurately quantify them in environmental matrices (Söderström et al., 2009; Munaron et al., 2012). As APIs are designed to be therapeutically active, the serious concern about the environmental fate related impacts in water quality status and potential effects on non-target organisms led to new EU and US legislative frameworks and directives (Roberts and Bersuder, 2006; Santos et al., 2010). Moreover, within the EU Water Framework Directive (WFD) out of the 41 priority substances listed, 14 are pesticides (Directive 2008/105/EC). Nevertheless, APIs and pesticides monitoring in natural waters is very complex due to their multiplicity in terms of e.g. physico-chemical properties, chemical structure and persistence in the environment (Castiglioni et al., 2004; Togola and Budzinski, 2007a).

The often called conventional aqueous matrices active screening methods (like, grab and pump sampling) present two major limitations: (i) the ability to provide an accurate time integrative estimation – only giving a snap-shot of contaminants present at the exact sampling time, often neglecting episodic environmental changes (such as accidental spills and seasonal variation) and (ii) the ability to quantify target analytes at ultra-trace and/or trace levels in discrete water samples (Petty et al., 2004; Alvarez et al., 2005; Togola and Budzinski, 2007a; Arditsoglou and Voutsa, 2008; Söderström et al., 2009). Even though these limitations can be overcome by the combination of multiple and repetitive time or with large volume of water samples, those are extremely costly and time consuming (Arditsoglou and Voutsa, 2008; Söderström et al., 2009; Togola and Budzinski, 2007a).

Passive samplers were conceived to tackle these limitations by reducing efficiently active sampling costs, maintenance and handling in water quality screening (Petty et al., 2004; Alvarez et al., 2005; Söderström et al., 2009). For further knowledge see reviews by Vrana et al. (2005) and Dévier et al. (2011) describing the broadly use, applications and current state of the art of passive sampling technology for waterborne organic and inorganic contaminants in environmental monitoring.

Two integrative passive samplers for the sequestering of ultra- to trace levels of organic contaminants mixtures in natural waters

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developed by US Geological Survey's Columbia Environmental Research Center (CERC) are referred as the semipermeable membrane device (SPMD) (US Patent, 5,098,573; Huckins et al., 1992, 1995) for hydrophobic organic compounds and the polar organic chemical integrative sampler (POCIS) (US Patent 6,478,961; Petty et al., 2002) for hydrophilic organic compounds. Both passive samplers are based on the exchange flow kinetics of organic compounds from the surrounding water to the device receiving solid-phase either by partitioning of non-polar compounds trapped in SPMD or by adsorption of polar compounds sequestered in POCIS until the equilibrium is reached (Vrana et al., 2005; Arditsoglou and Voutsa, 2008).

POCIS devices are generally used for sampling polar organic molecules ($0 < \log K_{ow} < 4$) with no limitation of the type of natural waters. Since their development, POCIS have been successfully applied in surface waters (lagoon, riverine and marine) and sewage effluents in the detection and quantification of numerous organic compounds like pharmaceuticals, polar pesticides, steroids, alkylphenols and hormones (Alvarez et al., 2004, 2005; Jones-Lepp et al., 2004; Petty et al., 2004; MacLeod et al., 2007; Mazzella et al., 2007, 2010; Togola and Budzinski, 2007a; Arditsoglou and Voutsa, 2008; Zhang et al., 2008; Harman et al., 2008a, 2008b, 2009; Martínez Bueno et al., 2009; Li et al., 2010a,b; Pesce et al., 2011; Munaron et al., 2012).

The major drawback associated to the application of passive samplers (particularly POCIS) is the necessity of calculating accurate concentrations and availability of each target-compound sampling rate (R_s) (L/day) pre-calibration data prior to its deployment enabling environmental water concentrations expression as ng analyte per L (Togola and Budzinski, 2007a; Li et al., 2010b, 2011). For this, each polar analyte R_S has to be determined through laboratory experiments using flow-through or static renewal microcosm exposure systems describing the exchange kinetics between water and the passive samplers (Togola and Budzinski, 2007a; Söderström et al., 2009). Nevertheless R_s depends on each compound physicochemical properties and environmental conditioning (e.g. water flow rate, temperature, pH, salinity, dissolved organic matter (DOM) and biofouling) (Roberts and Bersuder, 2006; Togola and Budzinski, 2007a; Söderström et al., 2009; Li et al., 2011). This limitation can be suppressed through the application of performance reference compounds (PRCs) like the ones added to receiving phase of SPMDs prior to deployment. PRCs release is afterwards measured and this difference enables *in situ* R_s appraisal (Huckins et al., 2002).

Considering the above, the objective of this study pertain the detection and quantification of APIs and pesticides concentrations in two different sites in the Arade River estuary (Portugal) using passive sampler devices: POCIS. These devices were deployed in both up and downriver sites (Fig. 1) to assess the impact of tourism increase in the summer months (August to October) on APIs and pesticides concentration changes due to the expected increase in WWTPs discharges caused by the threefold population increase during this period.

2. Materials and methods

2.1. Sites characterization

Located in Southern Portugal, Arade estuary is an important ecological and economic system that comprises an area of 987 km^2. Surrounded by saltmarsh river banks, Arade River estuary cross several urban areas such as Ferragudo, Parchal, Mexilhoeira da Carregação and Portimão includes an approximate of 66,000 inhabitants (INE, 2011), supporting a marina and a large commercial harbor. The major contamination sources derive mostly from municipal, industrial discharges and agriculture (orcharding and rice culture) runoffs, but also from activities associated with tourism, marine traffic and aquaculture.

The two sites selected in the Arade River estuary for POCIS deployment were: Site 1 (also referred as downriver site) located inside Portimão commercial harbor (mostly dedicated to large cruises docking) on the west margin in the vicinity of two marinas and a shipyard about 2 km from the river mouth (37°07′42.9″N, 8°31′50.8″W). Additionally, this site is under the influence to the North of Companheira WWTP (WWTP1) that serves Portimão city (55,614 inhabitants), Alvor (>6000 inhabitants) and Mexilhoeira

Fig. 1. POCIS deployment sites and WWTPs in Arade River estuary. *Source:* ArcGIS 9 ArcMap version.