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Occurrence of pharmaceuticals and personal care products in effluent-dominated Saudi Arabian coastal waters of the Red Sea

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HIGHLIGHTS

- PPCPs were analysed in seawater from coastal sites in Jeddah (Saudi Arabia).
- High levels of PPCP (>10 microg/L SUM PPCPs) revealed sewage effluent contribution.
- Even in background stations PPCPs were quantified.
- A first pattern comparison identified diffusive sources influencing background locations.

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ABSTRACT

The occurrence of selected pharmaceuticals and personal care products (PPCPs) and the pesticide atrazine were investigated in seawater samples collected from stations located at effluent dominated sites in the Saudi Arabian coastal waters of the Red Sea. PPCPs were analysed using solid phase extraction (SPE) followed by high performance liquid chromatography – tandem mass spectrometry (HPLC-MS/MS). A multi component method for the ultra-trace level quantification of 13 target PPCPs in Seawater was developed and validated for the here performed study. The method procedure is described in detail in the supplementary material section. 26 samples from 7 distinct locations (2 directly influenced by continuous sewage release) were chosen for the sampling of surface seawater. Based upon local sales information, 25 target substances (20 PPCPs, 4 pesticides and 1 stimulant) were chosen for the here reported method development. Thirteen PPCPs were detected and quantified in a total of 26 seawater samples. Metformin, diclofenac, acetaminophen, and caffeine were identified as the most abundant PPCPs, detected in maximum concentration higher than 3 μg/L (upper quantification limit for the here developed method). Concentrations were in the range of 7– >3000 (metformin), <LOQ – 2379 ng/L (acetaminophen) and 62– >3000 ng/L (caffeine). The contribution of direct sewage release on the PPCP levels detected was obvious, the target PPCPs were detected in the Al-Arbaeen and Al-Shabab coastal lagoons in high concentrations due to the low water exchange with the open sea and still ongoing sewage releases in the lagoons. Also, substantial amounts of antibiotics were detected in all samples. Levels and distribution profile of the detected PPCPs revealed high level release rates and give raise to concern on potential environmental risks associated with the here document long term exposure on the fragile coastal marine environment of the region but particularly in the nearby protected coral reef environment outside the harbour region of Jeddah.

1. Introduction

Pharmaceuticals and personal care products (PPCPs) are today considered as high priority environmental pollutants (Daughton and Ternes, 1999; Halling-Sørensen et al., 1998; Kümmerer, 2001). These compounds are found in sewage (Batt et al., 2008; Ternes,

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1998; Weigel et al., 2004), river water (Dai et al., 2015; Kolpin et al., 2002; Tan et al., 2015), groundwater (Del Rosario et al., 2014; Sacher et al., 2001), seawater (Weigel et al., 2001, 2004), and even drinking water (Carmona et al., 2014; Qiao et al., 2011). PPCPs are introduced into the environment through several routes but primarily by raw and treated sewage (Daughton and Ternes, 1999). The removal efficiencies of many PPCPs by conventional wastewater treatment processes are low (Kosma et al., 2014; Stasinakis et al., 2013). PPCPs do not need to be persistent for exhibiting hazardous effects. Due reported to high-volume continuous discharge into the receiving aqueous environment (pseudo-persistence), a long term exposure must be assumed (Daughton and Ternes, 1999).

PPCPs like benzodiazepines and UV- filter compounds were reported to bioconcentrate in marine organisms (Chen et al., 2015; Chu and Metcalfe, 2007; Gomez et al., 2012). Due to the biochemical design of PPCPs, a highly sensitive toxic response in the exposed organisms must be assumed for most of the target substances at environmentally relevant concentrations (Cortez et al., 2012; Gagné et al., 2006; Giltrow et al., 2009; Martin-Diaz et al., 2009; Nassef et al., 2010). However, environmental concentrations are usually far below the therapeutic effect concentrations for the respective PPCPs (Kummerer, 2001; Kolpin et al., 2002.

Therefore, sensitive analytical methods are required for investigating the occurrence and fate of these trace contaminants in seawater. Since PPCPs occur usually at ultra-low level concentration (ppq-ppt) in seawater, effective preconcentration in combination with highly sensitive detection methods (HPLC-MS is a prerequisite for the quantitative trace analysis of PPCPs in environmental samples (Arpin-Pont et al., 2016).

Due to country specific prescription regulations, water treatment and consumption profiles, the release and distribution pathways for PCCPs are characteristic for the respective nations and cannot be assessed sufficiently by extrapolation of earlier studies and other countries evaluations (Pal et al., 2010). Therefore, a country specific environmental assessment on the occurrence of PPCPs in the Saudi Arabian environment is required as proper basis for regulatory measures.

The Red Sea has a unique environment with relatively high surface water temperatures (22–34 °C) and salinity (36.5–41‰) due to its location in an arid region and limited water exchange with to the Indian Ocean (Rasul and Stewart, 2015). This unique marine environment is the basis for a unique ecosystem with high abundance of marine organism including coral reef, marine fish and mammals species. Saudi Arabia, situated on the coast of the eastern Red Sea.

Within Saudi Arabia, only 37% of the total wastewater produced is treated in sewage treatment plants (STP) (Qadir et al., 2010) though a target of achieving 100% sewage coverage by 2025 has been set for all cities with populations greater than 5000 inhabitants (KICP, 2012). Expecting a significant increase of Wastewater production in the coming years, water reuse is being considered to augment the water resources in addition to groundwater supplies within Saudi Arabia and other Middle Eastern and North African (MENA) countries (Drewes et al., 2012; Hamoda, 2004). Water reuse was increased from 123 million m^3/year in 2006 to 219 million m^3/year in 2010 in Saudi Arabia (Al-Jassim et al., 2015). Within Saudi Arabia, there are at least thirty major sewage treatment facilities (Drewes et al., 2012), the majority of them apply secondary treatment procedure (Al-Jassim et al., 2015).

The coastal city of Jeddah is currently the second largest city in Saudi Arabia with a current population of 4 million inhabitants. The coastline around this major city has been extensively affected by development (Ziegler et al., 2016). The current wastewater treatments facilities in Jeddah are currently charged over their recommended capacities and are, thus, insufficiently treating the receiving sewage (Ziegler et al., 2016). As a consequence, this overflow leads to extensive discharge of raw or partially-treated sewage into the coastal waters (Mudarris and Turkey, 2006). The above described ineffective direct sewage dumping in the coastal water of the Jeddah area has increased notably since 2002 after sewage disposal in the artificial sewage lagoons east of Jeddah was terminated, this caused important environmental problems (El Sayed et al., 2015).

Generally, very little is known about the occurrence and fate of anthropogenic pollutants in the waters off the Saudi Arabian coast. However, a recently published survey on the occurrence of organic environmental pollutant of emerging concern in effluent samples from Saudi Arabian waste water treatment facilities revealed potential continuous emission of PPCPs into the coastal Red sea (Alidina et al., 2014). Effluent concentrations in ng/L to µg/L range were detection for the target substances. Based upon these findings the here reported study was conducted to investigate the occurrence fate of priority PPCPs in the receiving coastal sea water of the Red Sea.

To our best knowledge, no scientific study is reported in the literature on the occurrence of PPCPs in the Saudi Red Sea coastal waters except the above-mentioned study on levels in direct effluences from Saudi Arabian wastewater treatment plants (Alidina et al., 2014.

Thus, an investigation of the occurrence of PPCPs in effluent-dominated coastal sea waters of the Red Sea is expected to add urgently needed scientific information for adequate national environmental assessments required for future regulative measures. This study aims at assisting in the assessment of new technological approaches for the replacement of the current outdated wastewater treatment technologies. Furthermore, the here presented data represent the first scientific evidence on the occurrence of PPCPs in the Red Sea Saudi Arabian surface coastal water.

2. Materials and methods

The quantification method was adjusted to the requirements of surface water analysis in Red Sea seawater. The details on the analytical method including Chemicals, equipment and procedures can be found in the Supplementary materials section.

2.1. Selection of analytes

The target analytes in this study were selected based on their previous detection in sewage effluent samples collected from Saudi Arabia (Alidina et al., 2014; Shraim et al., 2017). The 20 original target compounds in this study included:: i) pharmaceuticals: acetaminophen (ACE), amitriptyline (AMT), atenolol (ATN), carbamazepine (CBZ), ranitidine (RAN), chlorpheniramine maleate (CPN), metronidazole (MTD), sulfamethoxazole (SMX), trimethoprim (TMP), diclofenac (DCF), Warfarin (WAR), ciprofloxacin (CIP), captopril (CAP), simvastatin (SIV), fluoxetine (FLX), metformin (MET), cephalexin (CEP); ii), caffeine (CAF), iii) personal care products: methylparaben (MEP), triclosan (TRC); iv) pesticides: atrazine (ATZ), benzophenone (BEP), triclocarban (TRB); and *N*,*N*-diethyl-*meta*-toluamid (DEET). Four isotopically labelled compounds used as internal standards were included: acetaminophen-(ring-d4), atenolol-d7, ciprofloxacin-d8, and atrazine-d5. The complete information on the standards applied for the here reported study can be found in Table S1 (supplementary materials section).