# Occurrence of emerging contaminants in environmental surface waters and their analytical methodology – a review

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## ABSTRACT

A new concern about surface water quality is the occurrence of emerging contaminants that have being recognized as a new class of water contaminants such as antibiotics, hormones, pesticides, personal care products and pharmaceutical products. The occurrence of these contaminants in the aquatic environment and especially in surface water is a serious concern because this is usually the source of water for drinking water treatment plants (DWTP). This review provides a summary of the occurrence and the analytical methodology (extraction process, chromatography analysis, detection systems and ionization source) of emerging contaminant analysis in surface waters including rivers, lakes, creeks and wetlands for their analysis.

**Key words** | analytical methodology, chromatography analysis, emerging contaminants, extraction process, surface water quality

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## INTRODUCTION

The occurrence of emerging contaminants (ECs), also called micropollutants, is derived from different sources that could be anthropogenic as well as natural substances. These contaminants in waters are commonly at trace concentrations, ranging from a few nanograms per litre (ng/L) to several micrograms per litre (μg/L) (Luo *et al.* 2014). The presence of ECs in surface waters is mainly attributed to discharges of wastewater (Petrie *et al.* 2015; Ebele *et al.* 2017) because conventional wastewater treatment, based on activated sludge processes, exhibits limitations on their removal (Tran *et al.* 2018). The ECs include a long list of products used daily such as antibiotics, hormones, pesticides, personal care products (PCPs), and pharmaceuticals.

In particular, the occurrence of ECs in surface water could be a troubling problem when this is used for drinking water (Riva *et al.* 2018). These contaminants have been detected globally in many natural water systems including rivers, lakes and reservoirs (Wang *et al.* 2011; Lai *et al.* 2016; Wanda *et al.* 2017; Rivera-Jaimes *et al.* 2018). Since the end of the 19th century, drinking water supply has focused mainly on quality standards of microbial risk (WHO 2006), nevertheless there is a new concern about safe water access, that is, harmful chemicals in small amounts such as ECs. This contamination threatens surface water resources since water quality deterioration has become a serious concern worldwide due to the increase in pollution (John *et al.* 2014; WHO 2016; Wu *et al.* 2017).

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The number of ECs in the aquatic environment is growing continuously every year (Agüera *et al.* 2013) and its transformation products (TPs) continue to be an important aspect in this topic because TPs can often be more toxic than the parent compounds (Richardson & Ternes 2018). Considering the impact of these contaminants on aquatic life and human health, data analysis of these contaminants is required. This valuable and high-quality information can be supplied by sensible and selective analytical methods. Nevertheless there is still a gap in knowledge of occurrence, fate and effects in the environment. In this context, this paper investigated the data of EC occurrence in environmental surface waters and their detection methodology.

## EXTRACTION PROCESS

ECs are normally present at trace concentrations in surface waters requiring an extraction process called solid phase extraction (SPE). SPE is often needed to concentrate the target compounds for analysis. This technique is used by various researchers around the world. It follows USEPA method 3535A (USEPA 2007) and it is used in sample preparation for different purposes to remove interferences, for concentration or trace enrichment of the analytes, desalting and sample storage and transport (Agilent Technologies 2013).

The procedures for SPE, very similar for most organic analytes, are as follows: sample preparation, pH adjustment, setting up the extraction apparatus and information regarding extract concentration generally apply to all target analytes (USEPA 2007). Regarding the overall extraction step, SPE and solid phase microextraction (SPME) continue to be the main techniques for application in sample preparation before chromatographic analysis of ECs. SPME techniques have been developed not only for reduction of solvent and instrumentation extraction but also to improve and facilitate rapid and convenient sample preparation (Pawliszyn 2012).

According to the literature consulted, the most representative technology for extraction in the current analysis of ECs is SPE. This technique is used in multiple configuration columns for the detection of these contaminants. In the available literature on the application of SPE the hydrophilic-lipophilic-balanced (HLB) cartridge is widely used in the study of different CEs (Celle-Jeanton *et al.* 2014; Osorio *et al.* 2016; Rivera-Jaimes *et al.* 2018). Otherwise SPME technology has been employed by Regueiro *et al.* (2009) and Beceiro-González *et al.* (2007) to develop a methodology for the analysis of personal care products and pesticides in surface waters, respectively.

A new feature regarding SPME is the automation of the process, e.g. a method of automated SPME-GC-MS for the determination of pesticides in surface and ground water has been validated by Rodriguez-Lafuente *et al.* (2016). Also, new SPE materials have been developed as in fabric phase sorptive extraction (FPSE), a new device of very high sorbent loading in an ultra-thin coating (Kabir *et al.* 2017). These innovations represent new possibilities in the analysis of ECs in complex environmental samples such as those of surface waters.

## CHROMATOGRAPHY ANALYSIS

A rigorous evaluation of environmental pollution of ECs requires constant innovation in the analytical methodology. Moreover, the detection of ECs in the environment can be a challenge as they typically occur at trace concentrations. This difficulty encourages the development of analytical methods that are highly sensitive and selective. The principal analytical techniques for EC monitoring are mainly based on gas chromatography (GC) and liquid chromatography (LC) coupled to mass spectrometry (MS). In recent years, the tendency for analysis of ECs through liquid chromatography–tandem mass spectrometry (LC-tandem-MS) has increased. The extensive literature available confirms this choice of analysis for many classes of ECs in environmental samples, including surface waters (Spongberg *et al.* 2011; Afonso-Olivares *et al.* 2013; Celle-Jeanton *et al.* 2014; Torres *et al.* 2015; Aparicio *et al.* 2017; Munz *et al.* 2017; Wilkinson *et al.* 2017; Hermes *et al.* 2018; Rivera-Jaimes *et al.* 2018). This key technique for environmental analysis allows the detection of a wide range of polar and non-volatile compounds and can reduce sample preparation (Rosen 2007). Mass spectrometers use an ion source to generate ions with positive or negative charges (see

Ionization sources section). The ions then travel through the mass analyser and arrive at different parts of the detector according to their mass/charge (*m/z*) ratio, and hence ions can be identified (Ho *et al.* 2003).

As for gas chromatography–mass spectrometry (GC-MS), it remains a popular methodology since it is still considered a highly efficient separation technique, but lengthy sample derivatization processes are often required to ensure analyte volatility (Kanani *et al.* 2008), for instance derivatization or chemical modification. A great deal of literature about the monitoring of ECs in surface water that employs this technique (Bu *et al.* 2015; Kong *et al.* 2015; Selvaraj *et al.* 2015; Terzopoulou *et al.* 2015; Wang *et al.* 2015; Edjere *et al.* 2016; El-Gawad 2016) supports its analytical efficiency. Furthermore, GC still offers some clear advantages over LC, for instance higher separation efficiency and lower costs without the problems associated with the matrix effects of LC-MS/MS (Reemtsma & Quintana 2006).

The newest development to improve the separation of complex mixtures is multi-dimensional chromatography with dimensions based on different separation mechanisms (Leonhardt *et al.* 2015). Comprehensive two-dimensional gas chromatography (GC × GC) has been demonstrated as a technique capable of enhanced separation of compounds within a complex matrix (Organtini *et al.* 2014; Prebihalo *et al.* 2015) such as a sample of environmental water represents. Hence, many successful applications of GC × GC for EC detection in surface water have been addressed (Jover *et al.* 2009; Gómez *et al.* 2011; Wanda *et al.* 2017). The basic experiment of this technique comprises the connection of two chromatographic columns with complementary polarity that together enhance the separation capacity of the arrangement; the columns are interfaced through a modulator device, which effectively decouples elution on each column (Edwards *et al.* 2011; Tranchida *et al.* 2011).

Another aim in the methodologies for ECs is to improve the time for analysis and reduce the consumption of solvents. In this sense, a suitable choice is the use of chromatographic systems at very high pressure: ultra-high-performance liquid chromatography (UHPLC). This technique has gained importance in the analysis of ECs and many studies have employed this technique (Gros *et al.* 2012, 2013; Ma *et al.* 2016; Petrie *et al.* 2016; Yang *et al.* 2018). The use of this very high pressure together with 1.7-μm-particle-size columns allows savings on time and solvent consumption, without altering or even with improvements to sensitivity and peak resolution (Guillarme *et al.* 2007; Chauveau-Duriot *et al.* 2010).

## DETECTION SYSTEMS

High-resolution mass spectrometry (HRMS) combined with high-performance liquid chromatography is a technique that plays a role in the investigation of environmental processes and in the study of the fate of pollutants (Calza *et al.* 2013). One lauded benefit of HRMS is the possibility to retrospectively process data for compounds that has led to the archiving of HRMS data (Alygizakis *et al.* 2018). However the most important feature of HRMS is the capacity to determine the molecular formulas of the analytes from accurate mass measurements (Picó & Barceló 2015).

With regard to mass analysers, specifically hybrid instruments, QqToF, QqLIT and orbitrap for example are becoming more popular, because of their capabilities in achieving accurate mass measurements and acquiring indispensable qualitative information in the form of full-scan spectra (Petrovic & Barceló 2013). The actual literature on the analysis of ECs in surface waters shows the application of these hybrid mass analysers (Gros *et al.* 2012, 2013; Pitarch *et al.* 2016; Gago-Ferrero *et al.* 2017).

Nevertheless, MS may not be the only detection system for the analysis, from the large literature consulted in this review. Other methodologies based on different detection systems for the analysis of ECs have been recently published. Salvatierra-Stamp *et al.* (2015) reported EC analysis in water samples, including one river through a LC method coupled to a photodiode array detector (PAD).

## IONIZATION SOURCES

Different types of ion sources commonly used include, among others, electrospray ionization (ESI) and electron impact (EI). EI is by far the most commonly used ionization method for GC-MS instruments. Almost all the GC-MS methodologies for the analysis of ECs consulted in this review employed this ionization source. Nevertheless, ESI is today the most widely used ionization technique in chemical and biochemical analysis for liquid form samples because it ionizes molecules directly from the liquid phase (Wilm 2011). This soft ionization source uses electrical energy to assist the transfer of ions from solution into the gaseous phase without fragmentation (Ho *et al.* 2003; Banerjee & Mazumdar 2012). The extensive body of knowledge about the occurrence of ECs in surface waters confirms that this ionization source is the most widely used coupled to LC devices (Spongberg *et al.* 2011; Gros *et al.* 2013; Osorio *et al.* 2016; Hermes *et al.* 2018; Rivera-Jaimes *et al.* 2018).

## OCCURRENCE OF EMERGING CONTAMINANTS IN SURFACE WATERS AND THEIR ANALYTICAL METHODOLOGY

Despite the occurrence of ECs in surface water, numerous contaminants are still continuously released as a result of anthropogenic activities such as industry, agriculture and household activities and these may affect human health via exposure to drinking water (Hartmann *et al.* 2018). For this reason, the development of sensitive and reliable analytical techniques is essential for monitoring the occurrence of ECs in surface waters. A comparative analysis regarding the occurrence of ECs including pharmaceuticals, PCPs, pesticides, antibiotics and hormones in surface waters from several waterbodies and the methodology of detection are presented in this section. Table 1 summarizes the main analytical methodologies (extraction process, chromatography instrument, ionization mode and detection system) employed for the detection of diverse ECs in surface waters.

### Pharmaceuticals

In recent years, the growing occurrence of pharmaceuticals (both human and veterinary) has been referred to as one of the most imperative environmental concerns (Carmona *et al.* 2014; Hernández *et al.* 2014; Kosma *et al.* 2014). It is known that these contaminants occur widely in the environment of industrialized countries (Beek *et al.* 2016) as a result of the significant volume of pharmaceuticals that are used by humans for the treatment of diseases, injuries, or illnesses.

In surface waters of the USA, Deo (2014) (various authors, various methodologies) reported the occurrence of 93 pharmaceuticals including: antibiotics, antidepressants, antihypertensives, analgesics, and others. Félix-Cañedo *et al.* (2013) (SPE-GC-EI-MS/MS-tandem) reported the presence of pharmaceuticals in Mexico City's surface waters including ibuprofen, diclofenac, naproxen, gemfibrozil and ketoprofen, and also addressed the higher concentration of these pharmaceuticals than those found in groundwater. In the middle of Lake Geneva, one of the largest European lakes, 14 pharmaceuticals were regularly detected in concentrations up to 0.37 μg/L for 6 years (Chèvre 2014) (various authors, various methodologies). In surface waters such as streams, ponds and lakes of India the occurrence of 15 pharmaceuticals has been detected (Gani & Kazmi 2016) (various authors, various methodologies). Nannou *et al.* (2015) elucidated the occurrence of 23 pharmaceuticals at different sample points along the river Kalamas and Lake Pamvotis region of Eripus, Greece (SPE-LC-ESI-MS). Similar observations were reported in the surface waters of the river Allier, France, detecting nine pharmaceuticals (Celle-Jeanton *et al.* 2014) (SPE-UHPLC-ESI-MS-Q-ToF) and in Lake Dongting, China, 12 pharmaceuticals were identified at concentrations of a few ng/L to a hundred ng/L (Ma *et al.* 2016) (SPE-UHPLC-ESI-MS-Q-ToF).

In summary, human pharmaceuticals are released in aquatic systems due to anthropogenic activities; therefore, these contaminants have been detected in many surface waters and the highest concentrations are found in densely urbanized areas, where the aquatic system is highly impacted by urban wastewater (Margot *et al.* 2015). The measured concentrations of some relevant pharmaceuticals in different surface waters are listed in Table 2.

### Personal care products

PCPs include ingredients found in shampoos, washing lotions, skin care products, dental care products, sunscreen agents, cosmetics, perfumes etc. (Margot *et al.* 2015). Esters of *p*-hydroxybenzoic acid or parabens are a class of chemicals widely used as preservatives in cosmetics and pharmaceuticals (Guo *et al.* 2013). These compounds include bisphenol A and other esters such as methylparaben, ethylparaben, propylparaben etc. that have been used for decades

**Table 1** | Analytical methodologies employed for the detection of diverse ECs in surface waters

| Extraction process | Analytical methodology (chromatography instrument-Ionization source-detection system) | Compounds analysed | Reference |
|---|---|---|---|
| SPE | HPLC-ESI-MS/MS (tandem) | Pharmaceuticals, hormones, PCPs, plasticizers and perfluorinated compounds | Spongberg *et al.* (2011); Wang *et al.* (2011); Torres *et al.* (2015); Lai *et al.* (2016); Wilkinson *et al.* (2017); Rivera-Jaimes *et al.* (2018) |
| SPE | HPLC-ESI-MS (Orbitrap) | Pharmaceuticals | Calza *et al.* (2013) |
| SPE | HPLC-PAD | Eight ECs including carbamazepine, bisphenol A, 17$\alpha$-ethinylestradiol and triclosan | Salvatierra-Stamp *et al.* (2015) |
| SPE | UHPLC-ESI-MS/MS (tandem) | Pharmaceuticals, PCPs, illicit drugs and pesticides | Carmona *et al.* (2014); Celle-Jeanton *et al.* (2014); De Gerónimo *et al.* (2014); Ma *et al.* (2016); Paíga *et al.* (2016); Osorio *et al.* (2016); Petrie *et al.* (2016); Yang *et al.* (2018) |
| SPE | UHPLC-ESI-MS (QToF) | Pharmaceuticals, PCPs, artificial sweeteners, pesticides, and perflouroalkyl substances | Pitarch *et al.* (2016); Gago-Ferrero *et al.* (2017) |
| SPE | UHPLC-ESI-MS (QqLIT) | Pharmaceuticals and antibiotics | Gros *et al.* (2012, 2013) |
| SPE | GC-EI-MS/MS (tandem) | Pharmaceuticals, PCPs, antioxidants, pesticides, phenols, aromatic hydrocarbons etc. | Félix-Cañedo *et al.* (2013); Kong *et al.* (2015); Terzopoulou *et al.* (2015) |
| SPE | GCxGC-MS (ToF) | Pharmaceuticals, plasticizers, pesticides, benzothiazoles, benzotriazoles and benzosulfonamides | Jover *et al.* (2009); Wanda *et al.* (2017); Glinski *et al.* (2018) |
| SPME | GC-EI-MS (tandem) | Pesticides, parabens, triclosan and related chlorophenols | Beceiro-González *et al.* (2007); Regueiro *et al.* (2009) |
| SBSE | HPLC-ESI-MS/MS (tandem) | Polar and non-polar emerging and priority pollutants | Aparicio *et al.* (2017) |
| SBSE | GCxGC-MS (ToF) | Priority and emerging contaminants including: PCPs, pesticides, and aromatic hydrocarbons | Gómez *et al.* (2011) |
| LLE | HPLC- FD | | |

EI: Electron impact; ESI: Electrospray ionization; FD: Fluorescence detection; GC: Gas chromatography; GCxGC: Two-dimensional gas chromatography; HPLC: High-performance liquid chromatography; LC: Liquid chromatography; LLE: Liquid–liquid extraction; MS: Mass spectrometry; PAD: Photodiode array detector; Q: Quadrupole; QqLIT: Quadrupole linear ion trap; SBSE: Stir bar sorptive extraction; SPE: Solid phase extraction; SPME: Solid phase microextraction; UHPLC: Ultra-high-performance liquid chromatography; UPLC: Ultra-performance liquid chromatography; ToF: Time of flight.

(Czarczyńska-Goślińska *et al.* 2017). The occurrence of these compounds in surface water has been determined in several studies (Regueiro *et al.* 2009; Yamamoto *et al.* 2011; Renz *et al.* 2013).

Another compound used as an antimicrobial in soaps, deodorants, skin creams, toothpaste and plastics is triclosan, a biphenyl ether (McAvoy *et al.* 2002) that has been identified in surface water in many works of the consulted literature (Nishi *et al.* 2008; Lyndall *et al.* 2010; Bu *et al.* 2015; Petrie *et al.* 2016). Nonylphenol is an ultimate degradation product of nonylphenol polythoxylates that are also used in cleaning and industrial processes (Mao *et al.* 2012). This compound have been detected in some surface water (Jin *et al.* 2013; Kong *et al.* 2015; Terzopoulou *et al.* 2015; Cherniaev *et al.* 2016). The measured concentrations in surface water of bisphenol A, nonylphenol and triclosan, which are widely used in PCPs, are listed in Table 3.

## Pesticides

According to their use, pesticides are classified generally into four categories: fungicides, herbicides, bactericides,

**Table 2** | Occurrence of some relevant pharmaceuticals in different surface waters: main concentration and/or the highest concentration (in brackets)

| Compound | Concentration (ng/L) | Surface water location | Analytical methodology | Reference |
|---|---|---|---|---|
| Acetaminophen | 123 (156) | Pamvotis Lake and Kalamas River (Greece) | SPE-LC-ESI-MS | Nannou *et al.* (2015) |
| | 243 | Onya River (Spain) | SPE-HPLC-ESI-MS (QqLIT) | Gros *et al.* (2012) |
| | 3,422 (4,460) | Apatlaco River (Mexico) | SPE-HPLC-ESI-MS/MS (tandem) | Rivera-Jaimes *et al.* (2018) |
| | 20.8 | Hogsmill, Chertsey Bourne, and Blackwater Rivers (England) | SPE-HPLC-ESI-MS/MS (tandem) | Wilkinson *et al.* (2017) |
| | 17.8 | Dongjiang River (China) | SPE-UHPLC-ESI-MS/MS (tandem) | Yang *et al.* (2018) |
| | 56 | Missouri River (USA) | SPE-HPLC-ESI-MS/MS (tandem) | Wang *et al.* (2011) |
| Carbamazepine | 2.9 (5.8) | Allier River (France) | SPE-UHPLC-ESI-MS/MS (tandem) | Celle-Jeanton *et al.* (2014) |
| | 50.79 (63.36) | Llobregat River (Spain) | SPE-LC-ESI-MS (QqLIT) | Osorio *et al.* (2012) |
| | 29 | Mkomazane River (South Africa) | SPE-GCxGC-MS (ToF) | Wanda *et al.* (2017) |
| | 31.7 (214) | Lis River (Portugal) | SPE-UHPLC-ESI-MS/MS (tandem) | Paíga *et al.* (2016) |
| | 113 (325) | Pamvotis Lake and Kalamas River (Greece) | SPE-LC-ESI-MS | Nannou *et al.* (2015) |
| | 16 | Grand River (Canada) | SPE-LC-ESI-MS (tandem) | Hao *et al.* (2006) |
| Diclofenac | 49 (3,462) | Turia River (Spain) | SPE-UHPLC-ESI-MS/MS (tandem) | Carmona *et al.* (2014) |
| | (260) | Fyris River (Sweden) | SPE-UHPLC-ESI-MS (QToF) | Gago-Ferrero *et al.* (2017) |
| | (52) | Onyar River (Spain) | SPE-HPLC-ESI-MS (QqLIT) | Gros *et al.* (2012) |
| | 40 (230) | Dongting Lake (China) | SPE-UHPLC-ESI-MS/MS (tandem) | Ma *et al.* (2016) |
| | 146 (457) | Pamvotis Lake and Kalamas River (Greece) | SPE-LC-ESI-MS | Nannou *et al.* (2015) |
| | 1,115 (1,398) | Apatlaco River (Mexico) | SPE-HPLC-ESI-MS/MS (tandem) | Rivera-Jaimes *et al.* (2018) |
| Ibuprofen | 1,830 | Rakkolanjoki River (Finland) | SPE-LC-ESI-MS/MS (tandem) | Meierjohann *et al.* (2016) |
| | 380 | Onya River (Spain) | SPE-HPLC-ESI-MS (QqLIT) | Gros *et al.* (2012) |
| | 730 (1,106) | Apatlaco River (Mexico) | SPE-HPLC-ESI-MS/MS (tandem) | Rivera-Jaimes *et al.* (2018) |
| | 116 | Dongjiang River (China) | SPE-UHPLC-ESI-MS/MS (tandem) | Yang *et al.* (2018) |
| | 37.5 | Mississippi River (USA) | SPE-HPLC-ESI-MS/MS (tandem) | Wang *et al.* (2011) |
| | 53.7 (1,317) | Lis River (Portugal) | SPE-UHPLC-ESI-MS/MS (tandem) | Paíga *et al.* (2016) |
| Naproxen | 1,687 | Rakkolanjoki River (Finland) | SPE-LC-ESI-MS/MS (tandem) | Meierjohann *et al.* (2016) |
| | 14.24 (114.04) | Ebro River (Spain) | SPE-UHPLC-ESI-MS/MS (tandem) | Osorio *et al.* (2016) |
| | 2.95 (12.21) | Júcar River (Spain) | SPE-UHPLC-ESI-MS/MS (tandem) | Osorio *et al.* (2016) |
| | 3.9 | Dongting Lake (China) | SPE-UHPLC-ESI-MS/MS (tandem) | Ma *et al.* (2016) |
| | 278 | Turia River (Spain) | SPE-UHPLC-ESI-MS/MS (tandem) | Carmona *et al.* (2014) |
| | 3,990 (4,820) | Apatlaco River (Mexico) | SPE-HPLC-ESI-MS/MS (tandem) | Rivera-Jaimes *et al.* (2018) |

and insecticides (Meffe & de Bustamante 2014) and are the main source of pesticide contamination through surface runoff from agricultural areas and by means of wastewaters in urban areas (Cahill *et al.* 2011). Atrazine, the most commonly used corn herbicide in the United States (Lozier *et al.* 2012), has been detected in surface waters, (Byer *et al.* 2011; Kong *et al.* 2015; Székács *et al.* 2015). Glinski *et al.* (2018) reported the pesticide metolachlor is the most frequently detected in surface water from the wetlands of the USA. Lari *et al.* (2014) reported that the pesticide chlorpyrifos showed the highest concentration in the surface water of agriculture-intensive areas in Bhandara, India. The concentrations in surface waters of the pesticides atrazine, metolachlor and chlorpyrifos are listed in Table 4.

## Hormones and antibiotics

Hormones and antibiotics are other compounds of emerging concern in water environments. The primary origin of steroidal hormones in the aquatic environment is human and animal defecation. In the long run, the natural and engineered hormones and their metabolites finally reach wastewater treatment plants (Barreiros *et al.* 2016; Gogoi *et al.* 2018). The hormone 17$\beta$-estradiol is an endogenous

**Table 3** | Occurrence of bisphenol A, nonylphenol and triclosan in different surface waters: main concentration and/or the highest concentration (in brackets)

| Compound | Concentration (ng/L) | Surface water location | Analytical methodology | Reference |
|---|---|---|---|---|
| Bisphenol A | 83.9 (203.0) | Langat River (Malaysia) | SPE-GC-EI-MS | Santhi *et al.* (2012) |
| | (277.9) | Gizdepka River (Poland) | SPE-HPLC-FD | Staniszewska *et al.* (2015) |
| | 25 (151) | Jiyun, Hai, Duliu and Luann Rivers (China) | SPE-GC-MS/MS (tandem) | Kong *et al.* (2015) |
| | 62.3 | River water (England) | SPE-UHPLC-ESI-MS/MS (tandem) | Petrie *et al.* (2016) |
| | 159 | Hogsmill, Chertsey Bourne, and Blackwater Rivers (England) | SPE-HPLC-ESI-MS/MS (tandem) | Wilkinson *et al.* (2017) |
| | (7) | Water of dams (Mexico) | SPE-GC-EI-MS/MS (tandem) | Félix-Cañedo *et al.* (2013) |
| Nonylphenol | 565 (2,622) | Jiyun, Hai, Duliu and Luann Rivers (China) | SPE-GC-MS/MS (tandem) | Kong *et al.* (2015) |
| | 50 | Strymonas River (Greece) | SPE-GC-EI-MS/MS (tandem) | Terzopoulou *et al.* (2015) |
| | (1,240) | Surface sea water of Amur Bay (Japan) | LL-HPLC-FD | Cherniaev *et al.* (2016) |
| | 109.22 | Hai River (China) | SPE-GC-EI-MS | Jin *et al.* (2013) |
| | 288.75 | Yangtze River (China) | SPE-GC-EI-MS | Jin *et al.* (2013) |
| | (655) | Water of dams (Mexico) | SPE-GC-EI-MS/MS (tandem) | Félix-Cañedo *et al.* (2013) |
| Triclosan | 96.3 (163) | Grand River (Canada) | SPE-LC-ESI-MS/MS | de Solla *et al.* (2016) |
| | 105 | Dongjiang River (China) | SPE-UHPLC-ESI-MS/MS (tandem) | Yang *et al.* (2018) |
| | 1 | Turia River (Spain) | SPE-UHPLC-ESI-MS/MS (tandem) | Carmona *et al.* (2014) |
| | 3.5 | Liaohe River (China) | SPE-GC-EI-MS | Bu *et al.* (2015) |
| | 101 | River water (England) | SPE-UHPLC-ESI-MS/MS (tandem) | Petrie *et al.* (2016) |
| | 107.1 | River water (Spain) | SPME-GC-EI-MS (tandem) | Regueiro *et al.* (2009) |

**Table 4** | Occurrence of pesticides atrazine, metolachlor and chlorpyrifos in different surface waters: main concentration and/or the highest concentration (in brackets)

| Compound | Concentration (ng/L) | Surface water location | Analytical methodology | Reference |
|---|---|---|---|---|
| Atrazine | 183 (1,829) | Jiyun, Hai, Duliu and Luann Rivers (China) | SPE-GC-EI-MS/MS (tandem) | Kong *et al.* (2015) |
| | (1,650) | Wetland water (USA) | SPE-GCxGC-MS (ToF) | Glinski *et al.* (2018) |
| | 120 (3,910) | Great Lakes (Canada) | SPE-GC-EI-MS | Byer *et al.* (2011) |
| | (15,000) | Surface water (Hungary) | SPE-GC-EI-MS | Székács *et al.* (2015) |
| | (19) | Mijares River (Spain) | SPE-UHPLC-ESI-MS (QToF) | Pitarch *et al.* (2016) |
| | 130 (532) | Surface water in rural area (China) | SPE-UHPLC-ESI-MS/MS | Yu *et al.* (2018) |
| Metolachlor | 90 (1,830) | Great Lakes (Canada) | SPE-GC-EI-MS | Byer *et al.* (2011) |
| | (20) | Landgraben, Rhine and Moselle Rivers and Tegel Lake (Germany) | LC-ESI-MS (tandem) | Hermes *et al.* (2018) |
| | (10,500) | Wetland water (USA) | SPE-GCxGC-MS (ToF) | Glinski *et al.* (2018) |
| | (56,000) | Surface water (Hungary) | SPE-GC-EI-MS | Székács *et al.* (2015) |
| | 2,300 | Strymonas River (Greece) | SPE-GC-EI-MS/MS (tandem) | Terzopoulou *et al.* (2015) |
| | 348 (836) | Water well (Brazil) | SPE-GC-Nitrogen-phosphorus | Dores *et al.* (2008) |
| Chlorpyrifos | (410) | Surface water of agriculture area (India) | LLE-GC-MS | Lari *et al.* (2014) |
| | (3,700) | Black Rascal Creek | Not described | Zhang *et al.* (2012) |
| | 9,310 | Lakes adjacent to agricultural fields (Bangladesh) | LLE-HPLC-PAD | Hossain *et al.* (2015) |
| | (729.5) | Santa Clara River and Calleguas Creek (USA) | LLE-GC-ESI-MS (tandem) | Delgado-Moreno *et al.* (2011) |
| Benfluralin | (1,250) | Wetland water (USA) | SPE-GCxGC-MS (ToF) | Glinski *et al.* (2018) |
| Acetochlor | (6,300) | Surface water (Hungary) | SPE-GC-EI-MS | Székács *et al.* (2015) |
| | (166) | Jiyun, Hai, Duliu and Luann Rivers (China) | SPE-GC-EI-MS/MS (tandem) | Kong *et al.* (2015) |

sex hormone, while the hormone 17$\alpha$-ethinylestradiol is a highly potent receptor agonist used in oral contraceptives (Laurenson *et al.* 2014).

Similar to hormones, antibiotics are introduced to the aquatic environment mainly through wastewater (Szekeres *et al.* 2017). Many studies on the occurrence of hormones

**Table 5** | Occurrence of the hormones 17β-estradiol and 17α-ethinylestradiol and the antibiotics ciprofloxacin and erythromycin in different surface waters: main concentration and/or the highest concentration (in brackets)

| Compound | Concentration (ng/L) | Surface water location | Analytical methodology | Reference |
|---|---|---|---|---|
| 17β-estradiol | 3,700 | Swart River (South Africa) | SPE-UHPLC-PAD | Olatunji *et al.* (2017) |
| | 1.7 | Pearl River (China) | SPE-GC-EI-MS | Gong *et al.* (2009) |
| | (56) | Piracicaba River (Brazil) | SPE-HPLC-ESI-MS/MS (tandem) | Torres *et al.* (2015) |
| | 1.91 | Pontchartrain Lake (USA) | SPE-GC-MS | Wang *et al.* (2012) |
| | (1.56) | Yungang Lagoon (China) | SPE-GC-MS | Zhang *et al.* (2011) |
| | (19) | Streams in agricultural area (USA) | SPE-GC-MS | Velicu & Suri (2009) |
| 17α-ethinylestradiol | (100) | Piracicaba River (Brazil) | SPE-HPLC-ESI-MS/MS (tandem) | Torres *et al.* (2015) |
| | (0.43) | Yungang Lagoon (China) | SPE-GC-MS | Zhang *et al.* (2011) |
| Ciprofloxacin | (1,168) | Wiwi and Oda Rivers (Ghana) | SPE-HPLC-MS/MS | Azanu *et al.* (2018) |
| | 1.55 (20) | Llobregat River (Spain) | SPE-UHPLC-ESI-MS/MS (tandem) | Osorio *et al.* (2016) |
| | 1.12 (16.34) | Ebro River (Spain) | SPE-UHPLC-ESI-MS/MS (tandem) | Osorio *et al.* (2016) |
| | (740) | Surface water (Costa Rica) | SPE-HPLC-ESI-MS/MS (tandem) | Spongberg *et al.* (2011) |
| | 5.8 | Taihu Lake (Taiwan) | SPE-HPLC-ESI-MS/MS (tandem) | Lai *et al.* (2016) |
| | (60.3) | Baiyangdian Lake (China) | SPE-HPLC-ESI-MS/MS (tandem) | Li *et al.* (2012) |
| Erythromycin | 1.85 (12.66) | Llobregat River (Spain) | SPE-UHPLC-ESI-MS/MS (tandem) | Osorio *et al.* (2016) |
| | 1.29 (18.58) | Ebro River (Spain) | SPE-UHPLC-ESI-MS/MS (tandem) | Osorio *et al.* (2016) |
| | (1,149) | Wiwi and Oda Rivers (Ghana) | SPE-HPLC-MS | Azanu *et al.* (2018) |
| | 183 | Dongjiang River (China) | SPE-UHPLC-ESI-MS/MS (tandem) | Yang *et al.* (2018) |
| | 1.05 | Grand River (Canada) | SPE-PLC-ESI-MS/MS | de Solla *et al.* (2016) |
| | 3.4 | Lunghu Lake (Taiwan) | SPME-GC-EI-MS/MS (tandem) | Lai *et al.* (2016) |

in the aquatic environment (Torres *et al.* 2015; Olatunji *et al.* 2017) and antibiotics (Bu *et al.* 2013; Deo 2014; Burke *et al.* 2016; Azanu *et al.* 2018) have confirmed the presence of these compounds in surface waters. The concentration in surface waters of the hormones 17β-estradiol, 17α-ethinylestradiol and the antibiotics ciprofloxacin and erythromycin are listed in Table 5.

## SOME NEW EMERGING CONTAMINANTS

As a consequence of increasing industrial activities, concern over new ECs has increased, for instance, from hydraulic fracturing (also called hydro-fracking or fracking) in which millions of gallons of water and additionally surfactants, sand and chemicals (including biocides) are injected by high pressure deep into the ground to fracture shales and extract gas into horizontally drilled wells (Richardson & Ternes 2018). The consequence of this polluting activity could be a new source of ECs in the aquatic environment, such as in surface waters.

Some other groups of contaminants are also emerging, for instance, manufactured nanoparticles and treatment by-products. The challenge for the assessment of the environmental analysis of nanoparticles is in how to measure them because they cannot be filtered out using conventional processes (Sauvé & Desrosiers 2014). Regarding treatment by-products as from chlorination commonly used as disinfectant, a risk is posed as it may lead to formation of trihalomethanes and haloacetic acids (Fakour & Lo 2018).

## CONCLUSIONS

ECs have been detected in surface waters around the world, pharmaceuticals and PCPs being reported with the highest incidence in water bodies.

The techniques that have shown greatest extraction capacity for ECs are SPME and SPE, the latter being most used because of the good retention capacity of a wider polarity spectrum of analytes and less dissolvent consumption. Regarding chromatographic techniques, LC and GC are the most used techniques. Nevertheless, UHPLC should be mentioned as a recently reported and highly efficient technique in the detection of ECs since it allows improvement in the sensitivity and resolution of signals.

With regard to the detection of ECs, techniques have been used that couple to mass spectrometry due to its high sensitivity since the concentration of ECs in surface waters tends to be very low, although interestingly, detection by PAD has also been reported.

This review contains valuable information about ECs in surface waters and seeks to provide EC inventories in concise terms to the scientific community for the purposes of the analysis of ECs and drinking water management.

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