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Review

A review on environmental monitoring of water organic pollutants identified by EU guidelines

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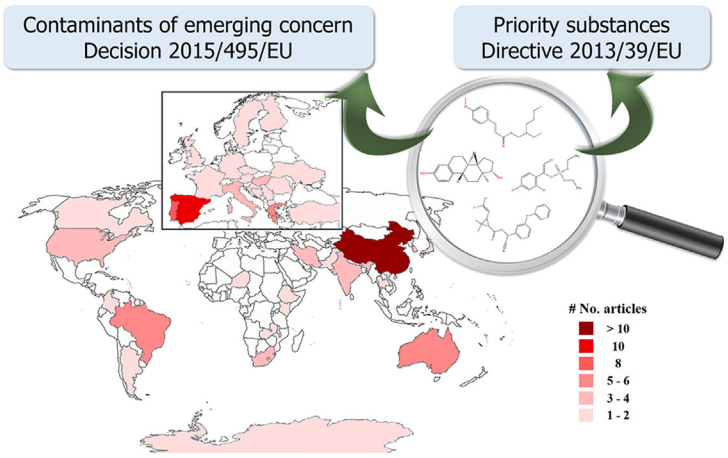
HIGHLIGHTS

- Occurrence of priority substances and contaminants of emerging concern is reviewed.
- Analytical methodologies, monitoring and sampling techniques are discussed.
- Four seasons, wet/dry, temporal or spatial monitoring of surface water are reviewed.
- Surface water chemical status needed for risk assessment, prevention and mitigation.
- The monitoring data reviewed may be useful for future regulations.

GRAPHICAL ABSTRACT



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ABSTRACT

The contamination of fresh water is a global concern. The huge impact of natural and anthropogenic organic substances that are constantly released into the environment, demands a better knowledge of the chemical status of Earth's surface water. Water quality monitoring studies have been performed targeting different substances and/or classes of substances, in different regions of the world, using different types of sampling strategies and campaigns. This review article aims to gather the available dispersed information regarding the occurrence of priority substances (PSs) and contaminants of emerging concern (CECs) that must be monitored in Europe in surface water, according to the European Union Directive 2013/39/EU and the Watch List of Decision 2015/495/EU, respectively. Other specific organic pollutants not considered in these EU documents as substances of high concern, but with reported elevated frequency of detection at high concentrations, are also discussed. The search comprised worldwide publications from 2012, considering at least one of the following criteria: 4 sampling campaigns per year, wet and dry seasons, temporal and/or spatial monitoring of surface (river, estuarine, lake and/or coastal waters) and ground waters. The highest concentrations were found for: (i) the PSs atrazine, alachlor, trifluralin, heptachlor, hexachlorocyclohexane, polycyclic aromatic hydrocarbons and di(2-ethylhexyl)phthalate; (ii) the CECs azithromycin, clarithromycin, erythromycin, diclofenac, 17α-ethinylestradiol, imidacloprid and 2-ethylhexyl 4-methoxycinnamate; and (iii) other unregulated

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organic compounds (caffeine, naproxen, metolachlor, estriol, dimethoate, terbuthylazine, acetaminophen, ibuprofen, trimethoprim, ciprofloxacin, ketoprofen, atenolol, Bisphenol A, metoprolol, carbofuran, malathion, sulfamethoxazole, carbamazepine and ofloxacin).
Most frequent substances as well as those found at highest concentrations in different seasons and regions, together with available risk assessment data, may be useful to identify possible future PS candidates.

Contents

1. Introduction

Water is a vital natural resource for humans, being also indispensable for all ecosystems. The water crisis already existing in some regions of the world may spread, resulting from the increasing water consumption and wasting, the irregular water world distribution, the climate changes that Earth is facing and the growing number of anthropogenic activities [1]. Moreover, the uncountable sources of production, use and disposal of numerous chemicals commonly employed in medicine, industry, agriculture, and even common household conveniences [2], led to the widespread occurrence of organic pollutants [3]. The uncontrolled discharge of such substances into the environment, even at trace concentrations (i.e., ng L^{-1} – μg L^{-1}, known as micropollutants), contributes to the accumulation of some of them in the aquatic compartments, with potentially detrimental effects to both aquatic ecosystems and human health [4–8].

In particular, regarding the occurrence of pharmaceuticals and estrogens, they reach the urban wastewater treatment plants (UWWTPs) through the sewage network [9], after metabolism and excretion as unchanged compounds or as metabolites, in urine and/or faeces. On the other hand, direct release may occur by improper dump of unused or expired drugs directly in toilet sinks or as solid waste [10]. Veterinary pharmaceuticals are used for pets, livestock and aquaculture, which excrete the parent drugs and their metabolites [6]. Agricultural activities are also important sources of micropollutants, particularly in the case of pesticides (insecticides and herbicides), since these substances are used to protect plants and improve productivity [11,12]. In addition, industrial compounds, many of them non-regulated in some regions of the world, are often directly released into surface water [13]. Even when industrial effluents are discharged into UWWTPs, most of these micropollutants are poorly removed [14]. In fact, it is consensual that effluents from UWWTPs are one of the main pathways for the introduction of micropollutants into the aquatic environment [13].

Conventional UWWTPs are not originally designed for elimination of organic micropollutants, some of them potentially toxic compounds, and their efficiency to eliminate this type of compounds is not yet clearly understood [15]. Considering the global large use and the well-known partial or complete resistance of most organic micropollutants to elimination in UWWTP, they are frequently detected in effluents, surface waters and tap water [16]. The lack of knowledge on the middle and/or long-term effects of micropollutants to ecosystems and human health [17] demands a precautionary behaviour due to chronic and long-term exposure [14]. The acute toxicity is less likely to occur than chronic toxicity resulting from long-term exposure, although easier to evaluate by toxicological assays. Ecotoxicological risk or hazard assessment [18] comprises evaluating the current status and changes that occur in organisms, due to their exposure to chemical contaminants and other stressors that may be present in the environment [19]. The continuous but non detected effects of these micropollutants may gradually accumulate, leading to irreversible changes on both wildlife and human health [20]. Moreover, several studies have reported that different compounds may have synergistic interactions leading to unexpected adverse effects to humans and other organisms [10,21]. Aquatic species have a major risk of exposure to individual agents and/or combinations of these compounds [14]; however, humans also depend on the fate and behaviour of micropollutants in surface and ground water used to supply the drinking water treatment plants [22].

Great technological advances of sensitive analytical instrumentation and methods for analysis of trace organic compounds have been done to accomplish the assessment of micropollutants occurrence in the environment, namely in fresh water resources [23]. Consequently, the number of reports on this subject tremendously increased in the last years (e.g., drugs, pesticides, personal care products, among others, in ground water, river water, sediments, soils and oceans) [13,24–26]. In fact, the environmental analysis of micropollutants is a complex challenge for analytical chemistry researchers, due to the complexity of matrices, the diversity of chemical properties of the analytes and their very low concentrations [27]. Nevertheless, the novel technologies developed in the last decade and the increased sensitivity of the available analytical instruments have extended the spectrum of compounds that can be determined [28].

The determination of organic pollutants in environmental samples is generally performed by liquid (LC) or gas (GC) chromatography, according to the volatility, polarity and thermal stability of the analytes [29]. Mass spectrometry is the detection method of choice due to the specificity and sensitivity and consequent undoubtedly identification and quantification with very low method detection limits [30]. The complexity of environmental matrices and the low concentrations detected in environmental samples, demand sample pre-concentration and removal of the interferences present in these samples, before chromatographic analysis [31]. Despite the drawbacks of solid phase extraction (SPE) such as the use of high volumes of organic solvents in comparison with miniaturized techniques, time consuming and high cost, it is still the most used technique due to the high enrichment factors and recoveries obtained, combined with the efficient reduction of interferences and matrix effects [32–34].

Regardless of the recognized sources and the numerous studies on occurrence of such type of pollutants, a consolidated knowledge about the current status of watercourses is missing [35].

1.1. European legislation

Water quality is one of the priority issues of the environmental policy agenda due to the increasing demand for safe and clean water. There are already some documents, identifying certain substances that should be monitored in order to provide mitigation measures whenever necessary. For instance, some European guidelines have been published since the year of 2000, when Directive 2000/60/EC was launched to establish a framework for Community action in the field of water policy [36]. This so-called EU Water Framework Directive (EU WFD) represented a huge improvement in the water protection policy, with the aim of achieving good ecological and chemical status of surface water. The EU WFD requires the EU Commission to identify priority substances/group of substances (PSs) with significant risk to or via the aquatic environment, and to set EU Environmental Quality Standards (EQS), defined as "the concentration of a particular pollutant or group of pollutants in water, sediment or biota which should not be exceeded in order to protect human health and the environment", obtained from chronic toxicity data for annual average value (AA-EQS) and from acute toxicity data for maximum allowable concentration (MAC-EQS).

EQS derivation relies on worst-case assumptions in order to guarantee environmental protection [37]. There are three methods for deriving EQS, the two main approaches are the probabilistic and deterministic methods and the other approach results from model ecosystem and field studies [37]. All these methods take into account the remaining uncertainty, by applying an assessment factor (AF), meaning that the resulting EQS are valid whatever the method employed [37]. Probabilistic methods adopt species sensitivity distribution (SSD) modelling, in which a distribution function is fitted to all reliable toxicity data (typically chronic no observed effect concentration (NOEC) or effect concentration for 10% of the individuals in a toxicity test (EC10)) as log values, from which a percentile is used for the EQS, usually 5th percentile (so-called HC5) representing the concentration below which at most 5% of all possible species are affected [37]. Although SSD models account for differences in sensitivity between species, a further AF is applied to the estimated HC5 to account for 'residual' uncertainties. SSD method should always be used in the cases where it is applicable and all approaches are generally performed when reliable data exist, i.e., EQS should also be derived by deterministic method and applying model ecosystems [37]. In those cases where all methods can be performed, the final value should be based on the results from the SSD method or the model ecosystem-studies, considering their more robust approach towards assessing ecosystem effects [37]. However, where the available data for a probabilistic approach is insufficient, the deterministic method is used. This approach also known as AF method, uses the lowest credible toxicity data (lowest credible NOEC/EC10 or LC/EC50) and applies an AF typical larger due to the uncertainties in the available experimental data [37]. The quantity and quality of data available determine the AF values used, which are proportional to the uncertainty.

In 2001, Decision 2455/2001/EC set the first list of 33 PSs that must be monitored at Community level, some of them marked as priority hazardous substances (PHSs), but the first list of EQS (AA-EQS and MAC-EQS) for the 33 PSs and 8 other certain pollutants, was only launched in Directive 2008/105/EC [38], which amended the EU WFD 2000/60/EC. A good chemical status of EU water bodies is achieved if the concentrations of PSs do not exceed the EQS. The member states must monitor the PSs in surface water and report the list of those which determined values exceed the respective EQS. EU WFD also highlights the need of specific measures to progressively reduce or phase out discharges, emissions and losses of PSs or PHSs, respectively.

In the same year of Decision 2455/2001/EC, the Stockholm Convention on Persistent Organic Pollutants (POPs) [39] was signed, aiming to eliminate or restrict the production and usage of POPs. The treaty was ratified in 2004, comprising a dozen of chemicals and the following agreements: 9 substances were highlighted to outlaw, the use of dichlorodiphenyltrichloroethane (DDT) was restricted to malaria control, and approaches to prevent the production or release of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/PCDF), hexachlorobenzene (HCB) and polychlorinated biphenyls (PCB) were included. The Stockholm Convention was adopted to EU legislation in EC Regulation No 850/2004 and there are 180 parties to the Convention (179 states and the European Union except Italy). United States, Israel and Malaysia, are not signatories.

Five years after the first list of EQS published in Directive 2008/105/EC, Directive 2013/39/EU [40] updated the previous documents. This Directive highlighted the demand to develop new water treatment solutions and recommended the monitoring of 45 PSs (41 organic PSs and the metals cadmium, lead, mercury and nickel) and a set of 8 other certain pollutants with EQS, totalizing 49 organic substances and 4 metals. Moreover, this Directive proposed a first Watch List of substances for Union-wide monitoring in the field of water policy, which was then published in Decision 2015/495/EU of 20 March 2015 [41]. The Watch List [41] contemplates 17 organic compounds defined as 10 substances/group of substances, so-called contaminants of emerging concern (CECs), unregulated pollutants for which Union-wide monitoring data need to be gathered for the purpose of supporting future prioritization exercises.

There are no EQS defined for CECs; however some authors [42] proposed a prioritization evaluation system based on two indicators, the frequency of exceedance and the extent of exceedance of Predicted No-Effect Concentrations (PNECs), which were applied to 500 contaminants classified into six categories identified by the Working Group on Prioritization of NORMAN Association, based on the quality and quantity of the available data [43]. These two indicators are based on maximum environmental concentrations (MEC) and on 95th percentile of the MEC at each site (MEC95) and compared to the lowest acute-based ($PNEC_{acute}$) or chronic-based ($PNEC_{chronic}$) thresholds [44,45]. In this approach, the frequency of sites which MEC exceeds the lowest PNEC gives insights on the spatial exposure, and the risk quotient RQ (MEC95/lowest PNEC) allows assessing the intensity of local impacts [42]. To better explain the risk levels, the RQs are classified into three risk levels: values below 0.1 indicate a low risk; $0.1 < RQ < 1$ represents a medium risk; and RQ above 1 reveals a high risk [46,47].

CECs comprise three large groups of compounds [13,48,49]: (i) substances that have been introduced into the environment

recently, such as new synthetic industrial compounds; (ii) compounds known for a longer time as present in the environment (e.g., hormones), but not before recognized as potentially dangerous to ecosystems and/or humans [50]; and (iii) compounds that have been detected using contemporary analytical techniques, despite being present in the environment for a long time. The continuous introduction of both PSs and CECs into environmental compartments turns them pseudo-persistent, increasing the potential to trigger off harmful effects. These substances come from industrial, medicinal and household usage, runoff from agriculture, livestock and aquaculture [51], being released worldwide into environmental compartments for decades [14,52]. Decision 2015/495/EU also includes the indication of the matrices to be monitored and possible methods of analysis for each substance/group of substances [41]. Decision 2015/495/EU [41] suggests the analytical method for each CEC included in the Watch List, with SPE coupled to LC-tandem triple quadrupole mass spectrometry (LC–MS/MS) being indicated for most compounds [41]. Nevertheless, SPE or liquid-liquid extraction (LLE) followed by GC coupled to mass spectrometry (GC–MS), is still preferential for some micropollutants, such as the CECs 2-ethylhexyl-4-methoxycinnamate (EHMC), 2,6-ditert-butyl-4-methylphenol (BHT), methiocarb, oxadiazon and triallate [41].

1.2. Contaminants of emerging concern (CECs) and priority substances (PSs)

This Section aims to introduce the substances of the Watch List of Decision 2015/495/EU and the PSs of the Directive 2013/39/EU. The Watch List comprises 5 pharmaceuticals, namely the non-steroidal anti-inflammatory drug (NSAID) diclofenac (Fig. S1a); the macrolide antibiotics (Fig. S1a) azithromycin, clarithromycin and erythromycin; and the synthetic estrogen 17α-ethinylestradiol (EE2), as well as the two natural estrogens estrone (E1) and 17β-estradiol (E2) (Fig. S1b). In recent years, the presence of pharmaceuticals and hormones in the aquatic environment has been considered an environmental concern [21] and consolidated data on their occurrence is crucial to suggest and develop new efficient treatment options in order to avoid or reduce their release into the environment. Since pharmaceuticals are designed with the purpose of having a biological effect, organisms living in aquatic ecosystems might be adversely affected by their release into the environment. In particular, NSAIDs are of great concern due to their wide administration in humans to treat inflammation and as pain relievers [16,53], being the largest group of over-the-counter drugs sold worldwide. A particular attention has also been given to antibiotics (e.g., macrolides) and hormones widely used in human and veterinary medicine, respectively due to their potential role in the development of resistant mechanisms by bacteria [54,55] and effects on endocrine system of organisms [56]. In some studies, where environmental risk assessment was carried out, the RQs determined in surface water were higher than 1 for many antibiotics, NSAIDs and hormones, indicating that these compounds could have adverse ecological effects [53,57–59].

The Watch List includes one antioxidant and one organic UV filter. BHT (Fig. S1c) is a highly active antioxidant applied as food additive [60], without an apparent direct risk to the environment. However, it is biodegraded to its metabolite 3,5-di-tert-butyl-4-hydroxybenzaldehyde, which was reported to generate peroxides in rats and to induce cellular DNA damage [60,61], making BHT a CEC of high concern. EHMC (Fig. S1d) is an organic UV filter identified in the Watch List, used as ingredient in sunscreens, as well as photostabilization agent in paints or polymeric materials [62–64]. Organic UV filters are normally resistant to degradation during water treatment processes and their lipophilicity promotes the bioaccumulation in the aquatic organisms and humans [64]. It is now known that large amounts of these potential endocrine disrupting substances [65,66] are released into the aquatic environment.

The number of publications about pesticides listed in the Watch List of Decision 2015/495/EU and also classified as PSs in Directive 2013/39/EU, increased in the last years due to their toxicity, persistence in the environment and bioaccumulation [19,67–70]. They can lead to the enhancement of incidence of cancer, genetic mutations and other diseases affecting mainly the liver or the central nervous system [13,71]. Various pesticides were already identified as inducers of toxic effects on primary producers [72]. The Watch List comprises 8 pesticides, namely 5 neonicotinoids (acetamiprid, clothianidin, imidacloprid, thiacloprid, thiamethoxam), a carbamate (methiocarb) and the 2 herbicides oxadiazon and triallate (Fig. S1e–g). Directive 2013/39/EU includes several pesticides (Fig. S2a–i): 4 triazines (atrazine, cybutryne, simazine, terbutryn); the chloroacetanilide alachlor; the dinitroaniline trifluralin; 2 diphenyl ethers (aclonifen, bifenox); various organochlorine pesticides (aldrin, isodrin, dieldrin, endrin, DDT total and p,p' – DDT, dicofol, endosulfan, heptachlor and its epoxide, HCB, hexachlorobutadiene, hexachlorocyclohexane and pentachlorobenzene); 3 organophosphorus pesticides (chlorfenvinphos, chlorpyrifos, dichlorvos); 2 phenylurea pesticides (diuron, isoproturon); the pyrethroid cypermethrin; and the quinoline quinoxyfen. Many of these pesticides (e.g., aldrin, DDTs, dieldrin, endrin) are considered POPs. In fact, contamination of surface and ground waters remains a problem even if these compounds were already phased out, since they were extensively used for decades [31] and also due to their illicit use, as suggested by their presence (or their metabolites) at high concentrations in the environment [73].

Directive 2013/39/EU also includes dioxins and dioxin-like compounds (Fig. S2j), PCDDs, PCDFs and dioxin-like PCBs (DL-PCBs), which are PSs that remain in the environment for several years, are toxic for most organisms and can bioaccumulate, originating dermal toxicity, carcinogenicity, reproductive, neurological and developmental toxicity [74]. Contamination of the aquatic compartments by these compounds may occur from direct discharge of waste containing dioxins into surface waters, or via indirect atmospheric inputs.

Some flame retardants (brominated diphenylethers and HBCDs) are PSs (Fig. S2k), since they are continuously released, transported through atmosphere and accumulated in the aquatic environment by wet and dry deposition [75], being reported in shellfish, birds and marine mammals [76].

Tributyltin (TBT) is a PS belonging to the organotin class (Fig. S2l), detected in marine and freshwater ecosystems at concentrations exceeding acute and chronic toxicity levels, which is used as antifouling agent in boat paints, disinfectant of circulating industrial cooling waters, slime control in paper mills and wood preservative [77].

Several industrial compounds such as phthalates (di(2-ethylhexyl) phthalate, Fig. S2m), alkylphenols (nonylphenol and octylphenol, Fig. S2n) and perfluorinated compounds (perfluorooctane sulfonic acid (PFOS) and its derivatives, Fig. S2o), are classified as one of the most severe environmental contaminants [78]. Some phthalates, alkylphenols and perfluorinated compounds are listed as PSs in the field of water policy [40] due to their high frequency of detection in the environment (at concentrations in the order of $\mu g\,L^{-1}$) [79], their toxicity, persistence and bioaccumulation ability [78,80,81]. Surface waters, mainly coastal and estuarine waters, are the most vulnerable environmental compartments to direct or indirect discharges of these contaminants, with illicit river discharges being recognized as a major source [82].

Polycyclic aromatic hydrocarbons (PAHs) (benzo(a)pyrene, benzo(b)fluoranthene, indeno(1,2,3-cd)-pyrene, benzo(k)fluoranthene, benzo(g,h,i)-perylene, anthracene, fluoranthene and

naphthalene, Fig. S2p) are an important class of PSs with fused aromatic rings, toxic and carcinogenic properties and relatively long lifetime in the environment, being able to react and originate polycyclic heteroaromatic hydrocarbons, including carbazole and furans [83,84]. Their occurrence can be related to natural processes as forest fires or can result from human activities, such as cigarette smoke and car exhaust fumes, production and processing of metals, coal, oil and gas [85].

Organic solvents (1,2-dichloroethane, benzene, carbon tetrachloride, dichloromethane, pentachlorobenzene, tetrachloroethylene, trichloro-ethylene, trichloromethane and trichlorobenzenes, Fig. S2q) are moderately volatile and lipophilic PSs, which may pose reproductive, developmental and cancer risks at trace levels [86]. C10-13 chloroalkanes (Fig. S2r), also known as short chain length chlorinated paraffins, are PSs of variable composition regarding to the chlorine content (up to around 70% by weight) and carbon chain lengths (between C10 and C13), toxic for wildlife [87] and mainly used as metal working fluids, sealants, flame retardants in rubbers and textiles, in leather processing and in paints and coatings [88].

1.3. Aim and scope

An increasing interest raised about the fate and effects of PSs and CECs, comprising a total of 66 organic pollutants with a wide range of chemical nature (49 PSs from Directive 2013/39/EU and 17 CECs from Watch List of Decision 2015/495/EU) [15,89]. This review aims to summarize relevant data of occurrence in surface and ground waters of organic pollutants specifically regulated in EU for surface water monitoring, namely 41 organic PSs and 8 other certain substances with EQS (i.e., a total of 49 organic compounds) defined in Directive 2013/39/EU (Section 2.2.1) and 10 substances/groups of substances (i.e., a total of 17 organic compounds) enlisted in the first Watch List for European Union monitoring, defined in the Decision 2015/495/EU (Section 2.2.2). The search comprised reports on micropollutants monitoring in Europe (Table S1) and worldwide (Table S2), published since 2012 in Scopus database (n = 137, accessed on 15th August 2017), using as keywords each organic PS (Directive 2013/39/EU) or CEC (Decision 2015/495/EU) and "ground water" (n = 15), "surface water" (n = 12), "river water" (n = 95), "estuarine water" (n = 15), "lake water" (n = 19) or "coastal water" (n = 10), some including more than one type of water matrix. Only studies dealing with at least (i) 4 sampling campaigns per year; (ii) wet and dry seasons; (iii) temporal monitoring (e.g., same sampling points in different years); or (iv) spatial monitoring (e.g., different locations), were considered. A total of 28 other unregulated organic compounds reported in these publications (different from the target PSs and CECs), even if they are not listed in the EU WFD, were also included in the separated Section 2.2.3 of this review.

2. Occurrence of PSs and CECs in surface and ground waters

The literature survey on monitoring programs of organic pollutants published since the beginning of 2012, shows that this research area has been increasing (Fig. 1), probably due to the higher concern of governmental entities and also the more sensitive analytical techniques available nowadays. A total of 137 publications were found using the defined search criteria (91 including PSs [4,18,19,24,56,58,68,73,74,78,81,83–85,90–166] and 77 including CECs [4,10,21,46,53,56–59,62,73,94,96,97,99,101,102,104,106,109–114,117–120,124,128,131,133,138,144,148,160,165,167–205], some of them including both PSs and CECs).

In general, the selection of sampling sites addresses the objective of providing relevant and representative data on the organic

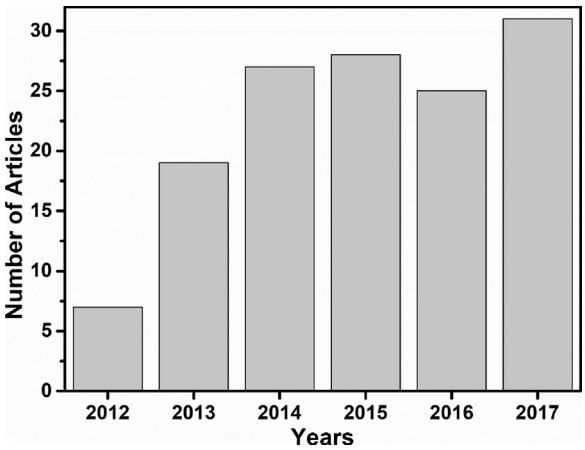

Fig. 1. Frequency of reports by year (2012 – 2017, up to 15th August 2017), dealing with monitoring of some of the 41 PSs, 8 other certain substances with EQS (Directive 2013/39/EU), and 17 CECs (Decision 2015/495/EU), discussed in this review article. The search was based on Scopus database using as keywords the name of each organic compound listed in the Directive 2013/39/EU or Decision 2015/495/EU and "ground water"; "surface water"; "river water"; "estuarine water"; "lake water" or "coastal water".

contamination and also attempts to investigate the influence of some anthropogenic practices [174]. Composition of environmental samples usually exhibits significant temporal and spatial variability [206]. Although some point or diffuse pollution emissions are generally constant or follow expected trends, variations of emissions into the water bodies are frequently observed, namely those reflecting seasonal changes (e.g., pharmaceuticals, UV filters, pesticides), as consequence of the production, usage or even release from other environmental compartments [206]. Different sampling strategies can be used, namely grab sampling and time-integrated sampling. Grab water sampling is the most used sampling technique, due to its easy and economic handling. In this case, monitoring programs of discrete grab samples allow obtaining data of contamination at an exact time and location. In turn, time-integrated sampling gives the average contamination over a longer period and is mostly performed using *in situ* passive sampling devices [206] that have the capability to collect a sample from a discrete location, without the active media transport induced by pumping or purge techniques [126]. Passive sampling allows gathering some micropollutants present at trace levels, without need to collect large volumes of water [207] and can be performed for long-term and spatial monitoring [90,126,208]. Manual composite sampling is other approach to get a time-integrated sample, given the main drawbacks of passive sampling, namely the influence of environmental factors (e.g., temperature, water flow rate, salinity) and the easy development of biofilms on the device's surface [209].

Spatio and temporal occurrence and distribution of micropollutants are affected by several factors, namely their input variations, the seasonality (weather conditions, temperature and consumption trends), the physicochemical properties of water, the water flow, biodegradation and photodegradation rates, among others [115,175]. In a study focused on the input of pharmaceuticals into watercourses, Moreno-González et al. [175] reported variations on the concentrations of macrolides and beta-blockers, which were related to seasonality, but also on elimination processes occurring in the environment such as degradation and sorption. Differences in water flows resulting from droughts and high evaporation rates (dry seasons) and seasonal rainfall (wet seasons) may be a governing aspect for the variability of micropollutants in rivers [104]. When rainfall leads to higher flows in a certain watercourse, it can originate hydrological phenomena like sediment re-suspension and dissolution of the compounds from other compartments (e.g.,

plants); however, this increase in the concentration can be hidden by the dilution phenomenon occurring simultaneously [59,176]. Conversely, the low flow verified in the dry seasons can originate higher concentrations of micropollutants, as verified for macrolide antibiotics [197]. Seasonal variations are not only related with the weather conditions, but also with the consumption patterns and input variations verified during certain periods of the year, which in turn also affect the spatial distribution of micropollutants. Important factors ruling the spatial distribution of micropollutants are the population density, the tourism and other anthropogenic activities circumscribed in certain locations, namely agriculture, livestock and industry [26,210]. For instance, the use of sunscreens causes higher concentrations of UV filters during holidays in the locations where they are mostly used, while the application of pesticides in crops increases during spring [26].

2.1. Monitoring studies by country

The world distribution of the reports considered in this review is represented in Fig. 2, as number of articles per country. Concerning the distribution per continents, 59 studies in 10 different countries of Asia were published [18,21,53,56,58,59,62,74,78,81,83,130–148,152–160,163,166,185–202], whereas 51 studies in 19 European countries were conducted [4,10,46,68,73,84,85,90–121,167–178]. Surface waters of the American continent were monitored in 13 studies, comprising 5 countries (Argentina [123,180], Brazil [57,127,128,182–184], Canada [129], Colombia [149], USA [164,165,205]). African water bodies were monitored in 4 countries, encompassing 7 studies (Ethiopia [150], Nigeria [19,161], South Africa [162,203,204] and Zambia [24]), whereas Oceania has only 4 monitoring studies conducted in Australia [124–126,181] since 2012, and Antarctica has only 2 reports [122,179]. For example, China [18,21,58,59,62,78,81,130–148,185–199] is the nominal leader of studies in the field of surface water monitoring, followed by Spain [73,115–120,175–177], Portugal [46,107–113] and Greece [97–101,172] (Fig. 2), according to the type of search done.

The world distribution of articles was also calculated normalizing the number of studies by the number of inhabitants (millions) of each country [211]. In this case, Spain, Portugal and Greece are the countries where monitoring campaigns of organic pollutants in surface water are most represented. Italy occupies the fourth position, followed by Hungary. Some case-study European sites include Ebro River [115,119], Llobregat River [52,118,176] and Guadalquivir River [116,120] in Spain; Lis River [46], Douro River [107], Guadiana basin [108], Tagus River [110], Mira River [111], Ave River [112] and Ria de Aveiro [113] in Portugal; Lake Vistonis Basin [97], surface waters of the region of Epirus [172], rivers and lakes of northern Greece [98,101], Pinios River Basin [99] and Acheloos River [100] in Greece.

2.2. Monitoring studies by substances

2.2.1. PSs

A considerable number (n = 91) of monitoring studies encompassing PSs [4,18,19,24,56,58,68,73,74,78,81,83–85,90–166] was found in the literature for the target period of time, in the following decreasing order: organochlorine pesticides (23.7%) > triazine pesticides (20.2%) > organophosphorus pesticides (11.6%) > PAHs (9%) ≈ alkylphenols (9%) > phenylurea pesticides (6.7%) > chloroacetanilide pesticides (3.7%) > perfluorinated compounds (3%) ≈ dinitroaniline pesticides (2.6%) > solvents (2.6%) ≈ dioxins and dioxin-like compounds (2.6%) > pyrethroid pesticides (1.9%) > flame retardants (1.5%) ≈ phthalates (1.5%) > organotins (0.4%), with at least one report per continent found. The most frequently worldwide studied PSs (from Directive 2013/39/EU) have been pesticides, namely atrazine, simazine, chlorpyrifos, terbutryn, diuron and alachlor (Fig. 3).

Concerning industrial compounds listed in Directive 2013/39/EU (Fig. 4), the perfluorinated compound PFOS was quantified in rivers of Southern England up to 119 ng L^{-1} [94] and up to 78.8 ng L^{-1} in ground water of Taiwan [56]. Solvents were referred in 2.6% of all articles reviewed, being pentachlorobenzene [116] and trichloromethane [130] referred in one study each, whereas trichloroethylene was reported in two publications [24,158], with a concentration of ca. 113 ng L^{-1} reported in Korea [158]. Regarding dioxins and dioxin-like compounds, PCDDs and PCDFs are not reported, but PCBs are monitored in some studies in Europe, up to 6.82 ng L^{-1} [90,91,93,101,105], as well as in Pakistan [137] and in China [74] up to 62.7 ng L^{-1}. The flame retardants polybrominated diphenyl ethers (PBDEs) were monitored in some studies [91,93,145], always below 0.16 ng L^{-1} and hexabromocyclododecanes ($\sum$HBCD, as sum of α- β- and γ-HBCD) were found at concentrations up to 2100 ng L^{-1} [157]. The PS di(2-ethylhexyl)phthalate was found in most of the samples analysed (93%) in China, up to 6350 ng L^{-1} [136], other studies conducted in China reporting higher values, up to 8840 ng L^{-1} [134] and 34200 ng L^{-1} [78]. Studies were not found for chloroalkanes (C10–C13), diphenyl ether pesticides and the quinoline pesticide quinoxyfen. As expected, in other environmental matrices such as sediments, some studies out of this scope were found [212–214]. Since these compounds are included in the list of PSs, monitoring campaigns are needed to understand their source and fate, as well as the negative effects that they can pose. Concerning substances with EQS defined in Directive 2013/39/EU, isodrin was not found in this literature review.

The PSs found at highest concentrations in this literature survey were PAHs, atrazine, di(2-ethylhexyl)phthalate, alachlor, hexachlorocyclohexane, trifluralin, heptachlor, trichloromethane, pentachlorophenol, cypermethrin, nonylphenol, naphthalene, diuron, endosulfan, fluoranthene, terbutryn, anthracene, HBCD, dieldrin, aldrin, simazine, dichlorvos, chlorpyrifos, DDT, and octylphenol (Fig. 4), all detected at least once at concentrations higher than 0.5 μg L^{-1}. Mean and median values for each substance were estimated respectively by the averages of the means and medians of the monitored concentrations, when these data were available in the reports (mean, median or all the values of determined concentrations); however, many studies do not provide enough data to calculate it. It is important to mention that the average of the available mean concentrations for each compound is generally higher than 130 ng L^{-1} (Fig. 4). Median values were not available for most studies, making difficult the comparison between different works.

The potential of PAHs for long-range transport, their persistent characteristics and the number of compounds encompassed, has provoked a great concern about them in the last years [84,149], also frequently reported in sediments [84]. PAHs were determined as their sum at high levels: up to 1208 ng L^{-1} in Raba River, Hungary [84]; up to 2160 ng L^{-1} in Czech Republic [93]; up to 1212 ng L^{-1} in China [141]; and up to 59.6 μg L^{-1} in Iran [154]. The contamination by this class of compounds was variable, since it depends on their structural nature and the monitoring season. In the Colombian Cauca River, PAHs were also detected up to 1901 ng L^{-1} [149]. In a study performed in Victoria's Yarra River, Australia, despite atrazine was detected at concentrations lower than 20 ng L^{-1} in 6% of the analysed samples, its metabolite desisopropyl atrazine was found at 1300 ng L^{-1} in 1% of the samples [125]. This was also observed in Spanish river water, where the concentrations of the metabolites desisopropyl atrazine and desethyl atrazine were found higher than those of the parent compound [73]. In turn, the same pesticide atrazine was detected at a maximum concentration of 5705 ng L^{-1} in Greece, in a study where chlorpyrifos was also detected up to 1011 ng L^{-1} in Pinios River and

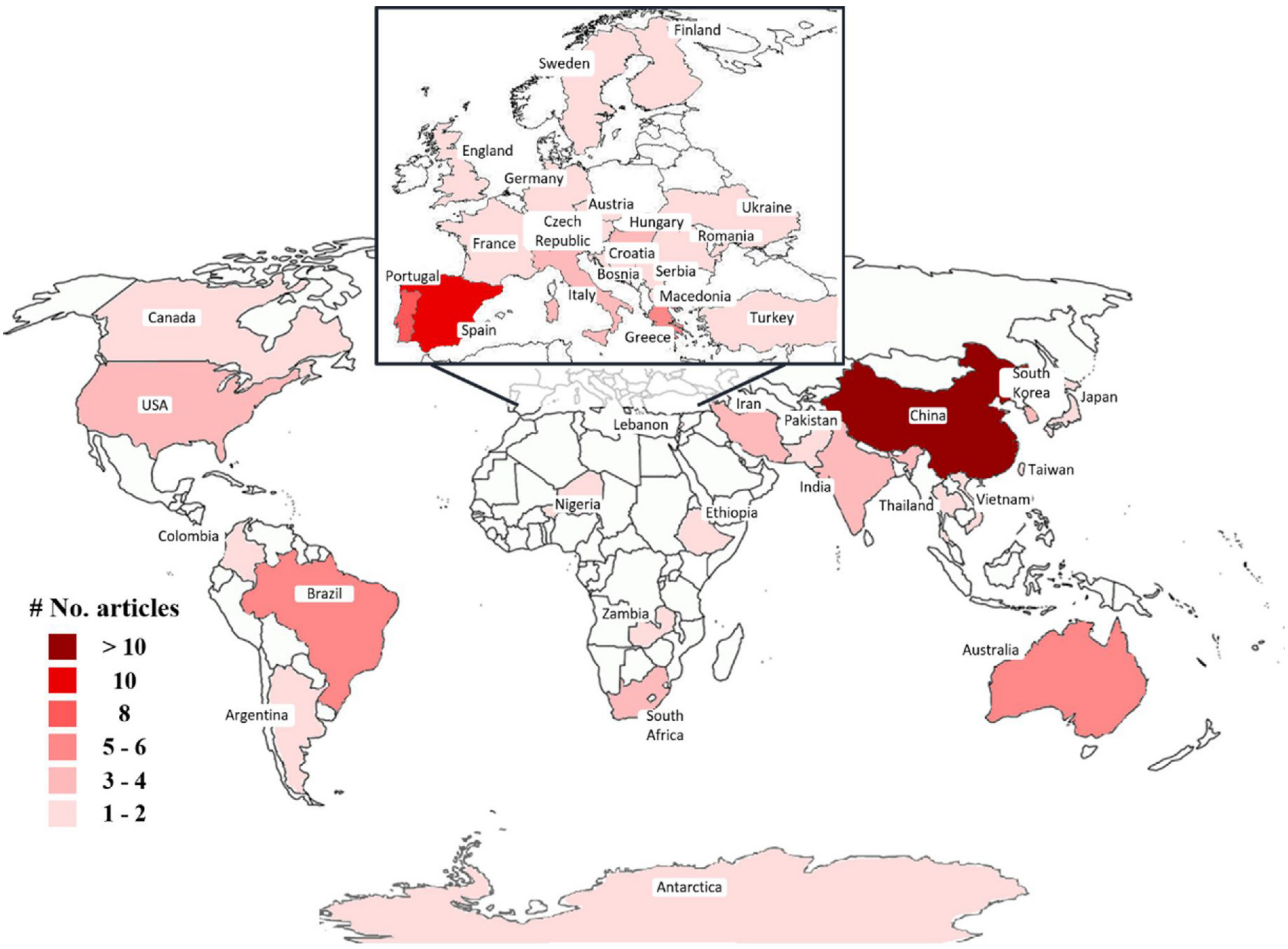

Fig. 2. Frequency of reports by country, published since 2012, dealing with monitoring of some of the 41 PSs, 8 other certain substances with EQS (Directive 2013/39/EU), and 17 CECs (Decision 2015/495/EU) discussed in this review article. The search was based on Scopus database using as keywords the name of each organic compound listed in the Directive 2013/39/EU or Decision 2015/495/EU and "ground water", "surface water", "river water", "estuarine water", "lake water" or "coastal water".

the overall frequency of detection was high, with 1037 positive samples of a total of 2382 samples [99]. In this study, trifluralin and endosulfan were also reported at high levels. Atrazine was also found between 500 and 15000 ng L^{-1} in different locations in Hungary, as well as the PSs trifluralin (10–10000 ng L^{-1}) and terbutryn (10–1000 ng L^{-1}) [102]. Simazine was quantified from draw wells in Brazil up to 1100 ng L^{-1} [128]. Dichlorvos was found at high concentrations (up to 1100 ng L^{-1}) in 23% of the 370 samples collected in Mae Sa watershed, Thailand, whereas cypermethrin was determined up to 500 ng L^{-1}, probably due to the intensive use on crops, such as bell pepper, chrysanthemum and white cabbage [163]. In a study performed between 2009 and 2011 in Karun River, Iran, several pesticides considered PSs were determined at high concentrations, namely: hexachlorocyclohexane (730–11121 ng L^{-1}), heptachlor (2079–9000 ng L^{-1}), aldrin (139–1474 ng L^{-1}), dieldrin (137–1775 ng L^{-1}) and total organophosphorus pesticides (22250–89340 ng L^{-1}) [156].

The presence of alachlor was reported at a concentration up to 271 ng L^{-1} in Pinios River (Greece), which was the highest concentration found in the 6 rivers under study [98]. More recently, in the same river, alachlor was found at levels up to 723 ng L^{-1} [99]. Other studies encompassed in this review reported concentrations below 20 ng L^{-1} [102,108]. In surface and ground waters of agriculture intensive areas from India, chlorpyrifos and dichlorvos were found respectively at a maximum concentration of 440 ng L^{-1} and 250 ng L^{-1} [152], probably because India is a country that has large scale manufacturing of chlorinated pesticides. In underdeveloped countries, such as Nigeria and Zambia, aldrin was reported at a mean concentration of 210 ng L^{-1} in Nigeria [19] and dieldrin at 140 ng L^{-1} in Zambia [24]. Nonylphenol, one of the most studied industrial compounds, was mainly included in monitoring programs also dealing with the endocrine disrupting hormones [110–113,133,148]. Nonylphenol was found in studies performed in China, in all the analysed samples, namely, in the Huangpu River at concentrations 20.2–1389 ng L^{-1} [133], in Haihe Plain at 165.8–1187.6 ng L^{-1} [144] and in Pearl River Delta between 34.3 and 3561 ng L^{-1} [18], where octylphenol was also determined up to 601 ng L^{-1}. Nonylphenol was also detected in Portugal, namely in Ria de Aveiro (up to 631 ng L^{-1}) [113] and in Tagus River estuary, Lisbon (up to 792 ng L^{-1}) [110]. Most of the monitoring campaigns addressed also the respective ethoxylates, which are usually found at higher concentrations than octylphenol and nonylphenol.

The maximum concentrations of PSs indicated in each monitoring program were compared to the respective EQS to estimate the risk. The concentrations of the following PSs exceeded the EQS values: atrazine [99,102,164], terbutryn [73,97,102], cypermethrin [99,123,163], fluoranthene [161,164], anthracene [149,161,164], diuron [73], tributyltin [147], dichlorvos [97,100,101,126,152,155,163,164], chlorpyrifos [97,99,100,123,128,152,163], pentachlorophenol [164], HCH [98,137,151–153,156], heptachlor [19,150,156], endosulfan [19,68,99,123,150,152,156,163], nonylphenol [18,131,164], HBCD [157] and alachlor [73,99]. Some studies were found in this literature survey, reporting at least 3 PSs with concentrations sur-

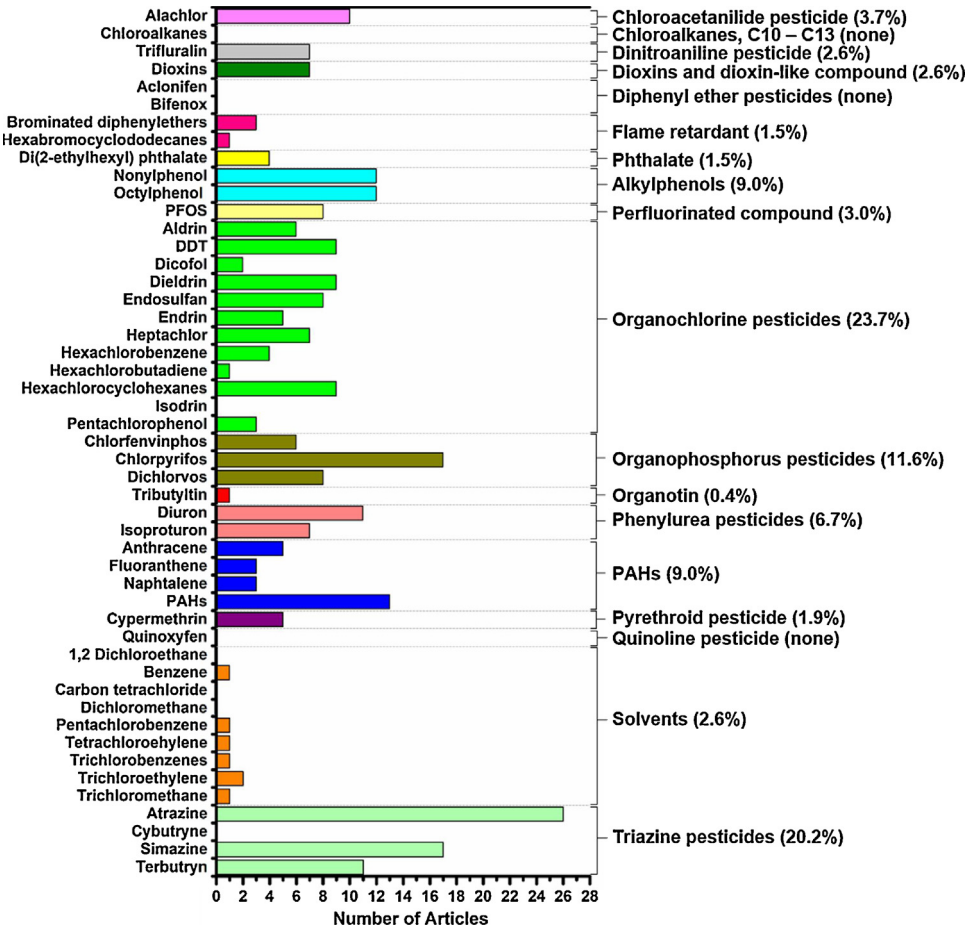

Fig. 3. Frequency of reports monitoring 41 PSs and 8 other certain substances with EQS (Directive 2013/39/EU), by substance and class of substances, published since 2012. The search was based on Scopus database using as keywords the name of each organic compound listed in Directive 2013/39/EU and "ground water", "surface water", "river water", "estuarine water", "lake water" or "coastal water".

passing the respective EQS in Greece [97,99], Spain [73], USA [164], Argentina [123], Thailand [163], India [152] and Iran [156]. Despite of some compounds being generally found at low concentrations, the concern about them should be considered, since the toxicity can be significant, leading to adverse effects to ecosystems even at very low concentrations [35].

2.2.2. CECs

Similarly to PSs, CECs from Decision 2015/495/EU have been included in the monitoring campaigns (n = 77) developed in the last years [4,10,21,46,53,56–59,62,73,94,96,97,99,101,102,104,106,109–114,117–120,124,128,131,133,138,144,148,160,165,167–205]. Pharmaceuticals represent the most studied class of Watch List compounds (42.9%). Among them, diclofenac is one of the most studied (17.7%), often within monitoring campaigns encompassing other pharmaceuticals and/or hormones, including those enlisted in the Watch List, such as estrogens [165,182] and macrolide antibiotics [172,176,200], the latter included in 25.2% of the reports of CECs herein reviewed. The natural estrogens E1 and E2 and the synthetic EE2 are the second most studied compounds enlisted in the Watch List, comprising 35.3% of the monitoring programs since 2012 (Fig. 5). This class was monitored in 5 continents [110,124,180,186,203] and pesticides (neonicotinoids and herbicides) were monitored in 4 continents [109,128,138,181]. Special attention should be given to imidacloprid since it is the most frequently studied Watch List pesticide in surface water samples with reported concentrations in Europe, as high as 656 ng L^{-1} in a study performed in Spain [73]. In Australia, it was found up to 4560 ng L^{-1} (Fig. 6) in a monitoring program encompassing the 5 neonicotinoids enlisted in the Watch List [181].

Only 2 out of 17 compounds of the Watch List (BHT and triallate) were not monitored (at least in surface and ground waters for the period considered in this literature survey). In fact, there are no published works on the occurrence of the food additive BHT in the last years, but it was monitored in two studies performed out of the period of the present survey, in USA [215] and Sweden [216], being respectively found at maximum concentrations of 49 ng L^{-1} and 620 ng L^{-1}. In any case, more monitoring campaigns are needed, in particular within Europe where they must be monitored, according to Decision 2015/495/EU.

Overall, the CECs included in the Watch List of Decision 2015/495/EU and analysed in the monitoring campaigns herein reviewed were determined at concentrations lower than those found for PSs. Moreover, half of CECs listed in the Watch List were detected up to μg L^{-1} levels (Fig. 6): EHMC up to 4043 ng L^{-1} in 93% of the analysed marine water samples in China [62] and up to 669 ng L^{-1} in Brazil [183]; imidacloprid in Australia up to 4560 ng L^{-1} [181] and in Rio Grande do Sul (up to 1660 ng L^{-1}) (Brazil) [128]; thiacloprid (up to 1370 ng L^{-1}) also in Australia [181]; EE2 up to 1822 ng L^{-1} [56]; diclofenac up to 7761 ng L^{-1} [179]; erythromycin up to 2806 ng L^{-1} [160], azithromycin up to 16633 ng L^{-1} and clarithromycin up to 2403 ng L^{-1} in Spain [175]. In a study performed in Spain [175], the highest values were observed during the weekends of spring and lower concentrations were registered during the rest of the week. Furthermore, azithromycin has been on the top of macrolides consumption, detected at

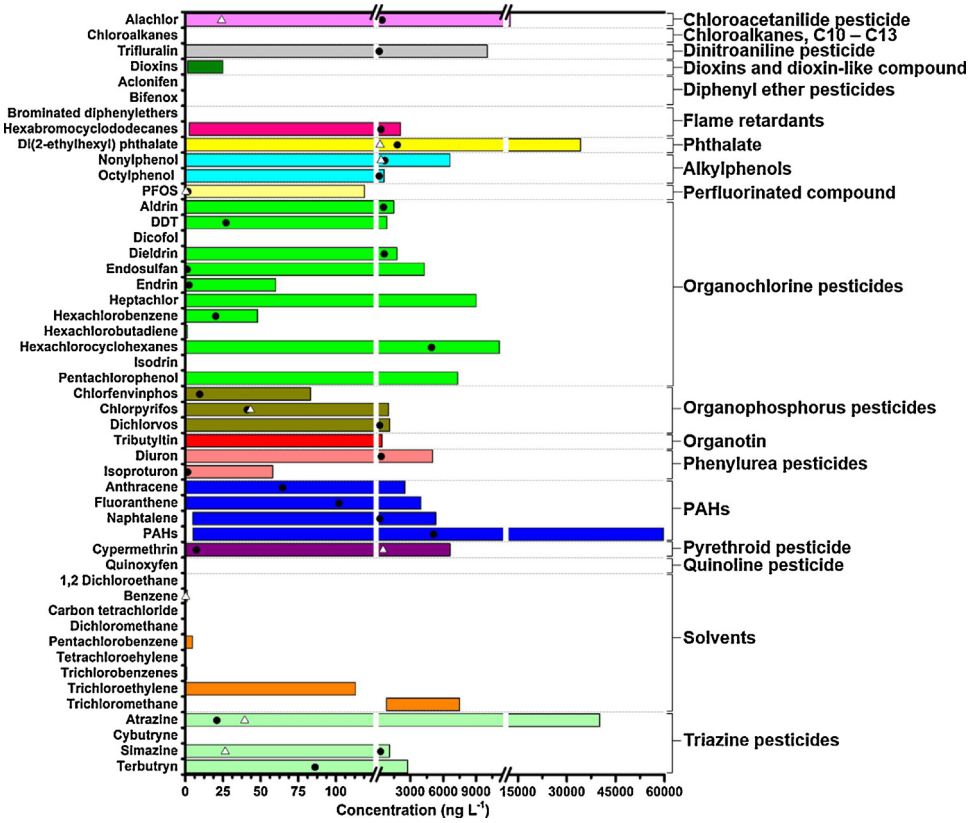

Fig. 4. Concentration range of the 41 PSs and 8 other certain substances with EQS (Directive 2013/39/EU) reported in the monitoring campaigns, published since 2012. The search was based on Scopus database using as keywords the name of each organic compound listed in Directive 2013/39/EU and "ground water", "surface water", "river water", "estuarine water", "lake water" or "coastal water". Mean (●) and median (△) values provided for each substance were estimated respectively by the averages of the means and medians of the monitored concentrations, when these data were available in the reports (mean, median or all the values of determined concentrations).

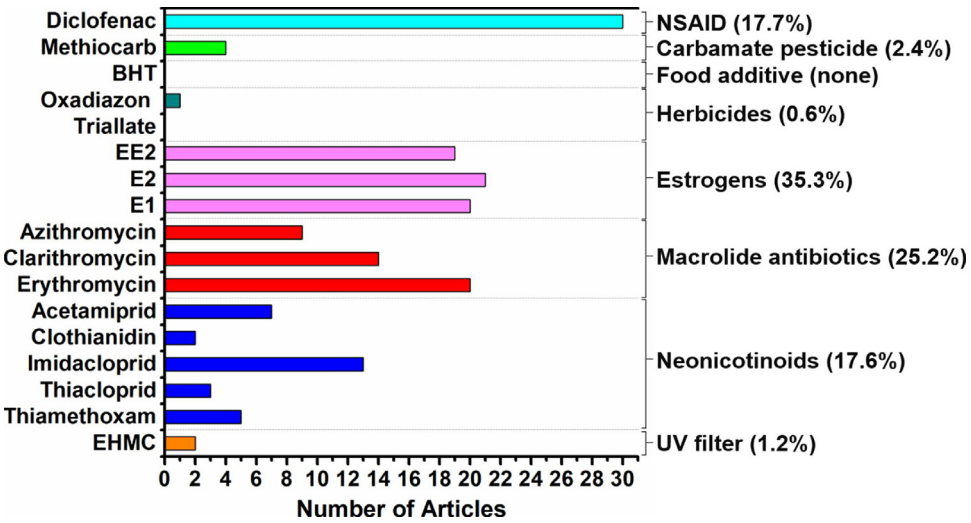

Fig. 5. Frequency of reports monitoring 17 CECs (Decision 2015/495/EU), by substance and class of substances, published since 2012. The search was based on Scopus database using as keywords the name of each organic compound listed in Decision 2015/495/EU and "ground water", "surface water", "river water", "estuarine water", "lake water" or "coastal water".

maximum concentrations of 4924 ng L^{-1} and 16633 ng L^{-1} in the winter and spring seasons, followed by clarithromycin that registered in the same study 2403 ng L^{-1} during winter season and 2121 ng L^{-1} during spring [175]. In general, the other studies here reviewed reported lower concentrations, below 100 ng L^{-1} for both azithromycin [4,46,190,194,195,198,205] and clarithromycin [190,194,195,198,205]. On the other hand, erythromycin was found at high levels, being the highest concentrations (2806, 1320 and 381.5 ng L^{-1}) found respectively in Lebanon [160] and China [194,196], the latter during spring in Shahu County of Jianghan Plain [194].

The highest concentrations of diclofenac were found in the Umgeni River system, KwaZulu-Natal South Africa (10200 ng L^{-1}) [204] and in Antarctica up to 7761 ng L^{-1} [179]. In the case of estrogens, EE2 and E2 were detected at 150 ng L^{-1} and 87 ng L^{-1}, respectively, in Piracicaba River (São Paulo, Brazil) [57]. The high-

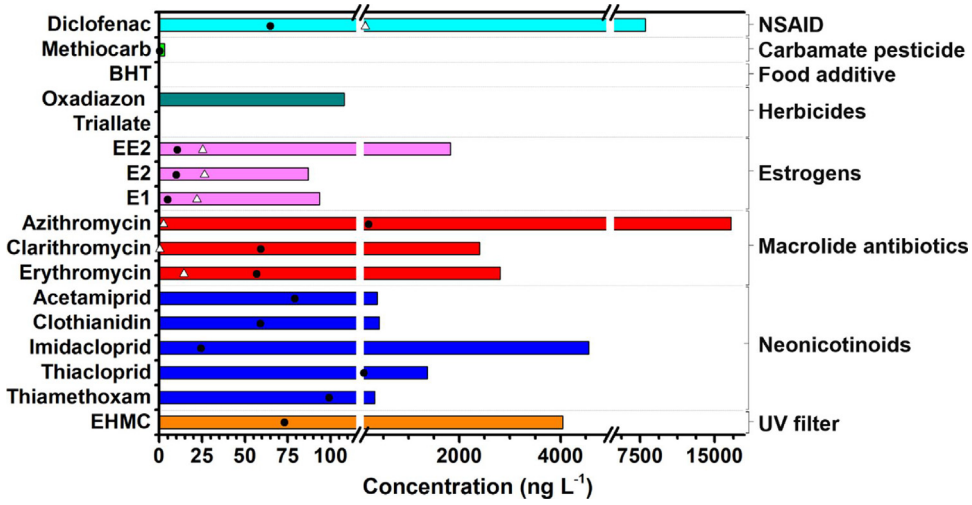

Fig. 6. Concentration range of the 17 CECs (Decision 2015/495/EU) reported in the monitoring campaigns, published since 2012. The search was based on Scopus database using as keywords the name of each organic compound listed in Decision 2015/495/EU and "ground water", "surface water", "river water", "estuarine water", "lake water" or "coastal water". Mean (●) and median (△) values provided for each substance were estimated respectively by the averages of the means and medians of the monitored concentrations, when these data were available in the reports (mean, median or all the values of determined concentrations).

est concentration found for EE2 was determined in Taiwan up to 1822 ng L^{-1} [56], whereas for E1 it was reported in Huangpu River, China (93 ng L^{-1}) [133]. Thiamethoxam, imidacloprid, thiacloprid and oxadiazon were found in Pinios River basin, Greece, at maximum concentrations of 330 ng L^{-1}, 306 ng L^{-1}, 120 ng L^{-1} and 108 ng L^{-1}, respectively [99]. Considering the widespread use of EHMC and the concentrations detected (up to 4043 ng L^{-1}) [62], more studies are needed on its occurrence [183].

The maximum concentrations measured in each study and the PNEC described elsewhere [45] were used to estimate the RQ. Values higher than 1 were obtained for: diclofenac [10,21,46,53,56,94,96,109,131,165,167,169,170,172,174–177,179,180,182,187,196,200,204], erythromycin [10,59,160,172,175,176,185,188,190,194,196,197], E1 [10,56,57,104,110–113,124,133,144,180,182,199], E2 [10,57,104,110–113,124,133,144,165,182,199,205] and EE2 [10,56,57,110–113,124,133,173,186,199]. In the case of clarithromycin [175,196,200] and azithromycin [175], RQ values higher than 1 were estimated for three and one studies, respectively. Some studies were found in this literature survey, reporting at least 3 CECs with concentrations exceeding the respective PNECs in Spain [175], Portugal [110–113], Turkey [10], Brazil [57,182], Taiwan [56] and China [196,199]. One of these reports refers to the 3 macrolide antibiotics [175] and several to the 3 estrogens [10,57,110–113,124,133,199]. However, a single potential risk (RQ > 1) is not enough to include a certain compound in the present directives. A broader risk analysis for prioritization of chemicals is needed, considering spatiotemporal variations, in order to understand whether the compounds reported frequently and at high concentrations, should be included in the present guidelines.

2.2.3. Other organic contaminants

As above mentioned, the compounds out of the scope of this search (not included in Directive 2013/39/EU or Decision 2015/495/EU), but detected in the collected reports (n = 88), were also encompassed in this review specifically for compounds included in 10 papers at least (Fig. 7) [4,10,19,21,24,46,53,56–59,62,73,78,92–94,96–102,104,106,108–114,116–120,124–134,136,138,144,147,148,152,155,156,158–160,162–165,167–180,182–205]. It was concluded that 28 organic compounds not listed in the EU legislation, are included in much more reported monitoring programs (Fig. 7) than some CECs and PSs, namely pharmaceuticals: antibiotics (35.2%, including ciprofloxacin, enrofloxacin, norfloxacin, ofloxacin, roxithromycin, sulfadiazine, sulfamethazine, sulfamethoxazole and trimethoprim), NSAIDs (13.9% represented by ibuprofen, ketoprofen, naproxen), beta-blockers (4.9%, including atenolol and metoprolol), lipid regulators and statin drugs (5.4% represented by bezafibrate and gemfibrozil), the psychiatric drug carbamazepine (6.0%) and the analgesic acetaminophen (3.2%); pesticides (20.3%, including carbofuran, metolachlor, carbendazim, diazinon, dimethoate, malathion and terbuthylazine); Bisphenol A (4.9%); the CNS stimulant caffeine (3.9%); and the estrogen estriol (E3) (2.3%).

From the 28 organic compounds not listed in the European documents which have been greatly monitored at high concentrations, most were detected at concentrations above 500 ng L^{-1} (Fig. 8); therefore more research about occurrence, fate and effects is also needed for many of these emerging compounds.

The most reported antibiotic herein reviewed was sulfamethoxazole, being reported up to 1820 ng L^{-1} in Taiwan [56]. In Beijing, China, the antibiotic trimethoprim, the second compound most reported in this review, was found in most analysed samples (96%) up to 13600 ng L^{-1} [190] and ofloxacin was found up to 990 ng L^{-1} [188]. In a study performed in the Buyukcekmece Watershed, Turkey, the pharmaceuticals ciprofloxacin (up to 13576 ng L^{-1}, the maximum concentration herein described), amoxicillin (up to 1654 ng L^{-1}) and naproxen (up to 12300 ng L^{-1}) were the compounds detected at highest concentrations, together with caffeine (up to 5525 ng L^{-1}) [10]. The higest concentrations of the three NSAIDs ketoprofen (9220 ng L^{-1}), naproxen (59300 ng L^{-1}) and ibuprofen (17600 ng L^{-1}) were found in South African surface waters [204]. In a study conducted in Finland, four pharmaceuticals were detected in the Rakkolanjoki River at concentrations ranging from ng L^{-1} levels to more than 1 μg L^{-1} (carbamazepine up to 1705 ng L^{-1}, the maximum concentration here reported; naproxen up to 1687 ng L^{-1}; ibuprofen up to 1830 ng L^{-1}; and metoprolol up to 1326 ng L^{-1}), whereas the CEC diclofenac was detected up to 700 ng L^{-1} [169]. In a study performed in Epirus, Northwestern Greece [172], caffeine (125–3506 ng L^{-1}) and salicylic acid (up to 3001 ng L^{-1}) were detected in all the samples (n = 32), whereas ibuprofen was also found at high concentrations in 81% of the tested samples (up to 1351 ng L^{-1}). In the Lis River, Portugal, ibuprofen was detected (up to 1317 ng L^{-1})

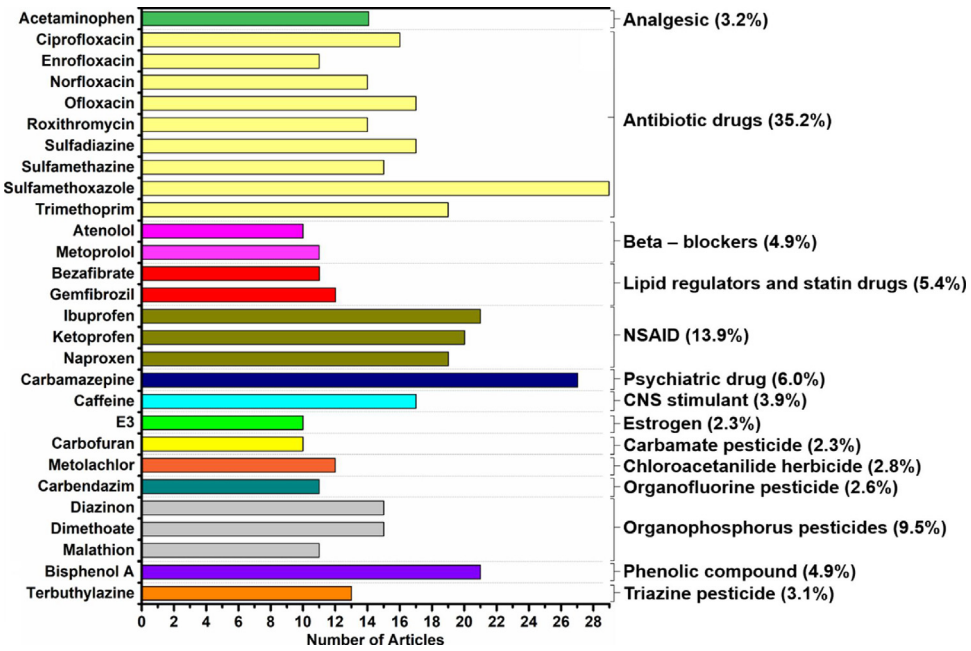

Fig. 7. Frequency of reports monitoring other organic substances within the papers reviewed dealing with CECs (Decision 2015/495/EU), PSs or other certain substances with EQS (Directive 2013/39/EU), by substance and class of substances, published since 2012 and discussed in this review. The search was based on Scopus database, using as keywords the name of each organic compound listed in the Decision 2015/495/EU or Directive 2013/39/EU and "ground water", "surface water", "river water", "estuarine water", "lake water" or "coastal water".

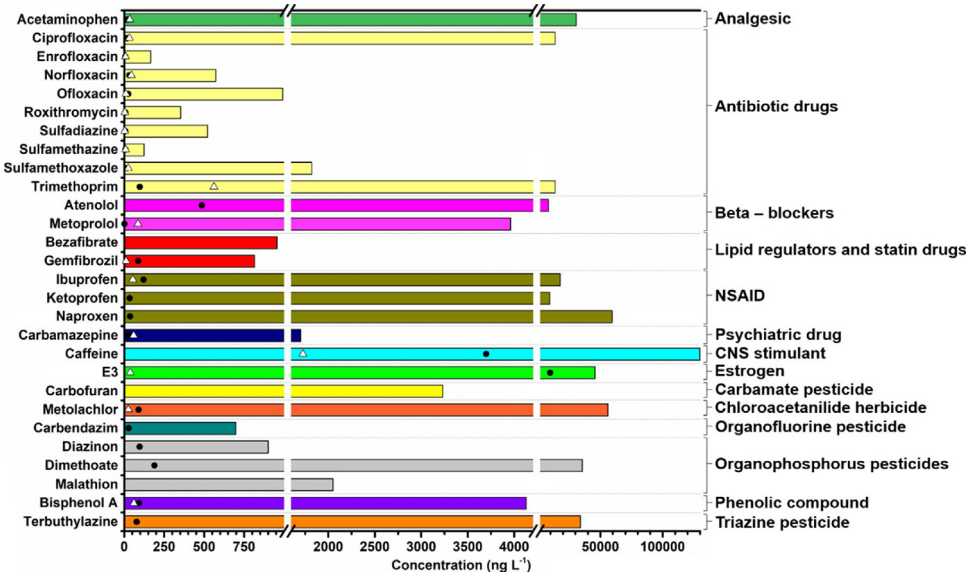

Fig. 8. Concentration range of the other organic substances reported in the monitoring campaigns reviewed dealing with CECs (Decision 2015/495/EU), PSs or other certain substances with EQS (Directive 2013/39/EU), published since 2012 and discussed in this review. The search was based on Scopus database, using as keywords the name of each organic compound listed in the Decision 2015/495/EU or Directive 2013/39/EU and "ground water", "surface water", "river water", "estuarine water", "lake water" or "coastal water". Mean (●) and median (△) values provided for each substance were estimated respectively by the averages of the means and medians of the monitored concentrations, when these data were available in the reports (mean, median or all the values of determined concentrations).

in all the 55 analysed samples [46]. Ibuprofen was also found at high concentrations (up to 5291 ng L^{-1}) in a study performed in Spain, acetaminophen being also detected at high levels, up to 9606 ng L^{-1} [175], as reported in other study developed in Guadalquivir River, Spain, which described this analgesic in 46% of the analysed samples, with mean concentrations of 979.6 ng L^{-1} [116]. In the Monjolinho River (São Paulo, Brazil) the concentration of acetaminophen was determined up to 30421 ng L^{-1} (77% of the samples) and atenolol up to 8199 ng L^{-1} (76% of the samples) [182], the highest concentrations herein reviewed for both pharmaceuticals (Fig. 8). Another monitoring campaign performed in Llobregat River and Sant Joan Despí (Spain) showed high concentrations of five pharmaceuticals, namely acetaminophen (4.4–1060 ng L^{-1}), sotalol (0.1–3553 ng L^{-1}), sulfamethoxazole (0.2–1500 ng L^{-1}), hydrochlorotiazide (up to 2436 ng L^{-1}) and metoprolol (0.1–3960 ng L^{-1}, the maximum concentration herein reviewed) [176].

Regarding pesticides, dimethoate was detected at a mean concentration of 1908.6 ng L^{-1} in 27% of the analysed samples of Guadalquivir River and other related surface waters in the province

of Jaén, Spain [116]. Dimethoate was found at 35440 ng L^{-1} in a study where carbofuran, linuron, chlorothalonil and metalaxyl were reported at concentrations higher than 2 μg L^{-1}, in the Maritime Region of Canada [129]. The pesticide metolachlor was detected at 56000 ng L^{-1} in Hungary [102]. Terbuthylazine was found up to 34.0 μg L^{-1} in Spain [73] and up to 31.5 μg L^{-1} (62% of the 270 samples) together with fluometuron determined up to 317.6 μg L (92%) in Lake Vistonis Basin, Greece [97].

Caffeine was one of the compounds most frequently reported in the literature and found at highest concentrations. It was found in the Monjolinho River (São Paulo, Brazil), with a frequency of 92% and concentrations up to 129585 ng L^{-1} [182]. Although caffeine and acetaminophen have high PNEC values, they can pose adverse ecotoxicological effects [217], especially when present as mixtures [7]. Caffeine was also detected in all samples of two studies performed in China, at concentrations between 31.3 ng L^{-1} [196] and 8095 ng L^{-1} [21], both in the Beiyun River of Beijing. In one of these studies [196], acetaminophen and caffeine were also found respectively up to 3577 ng L^{-1} and 2714 ng L^{-1}, whereas erythromycin was determined up to 1320 ng L^{-1} and N,N-diethyl-m-toluamide up to 1356 ng L^{-1}. In a study performed in 109 major Japanese rivers and some tributaries, caffeine was detected at concentrations up to 2400 ng L^{-1} in 87% of the analysed samples and sulpiride was determined up to 1400 ng L^{-1} with a detection frequency of 61% [200].

Other substances were found in the literature with less reports, but at very high concentrations. As example, tris(1-chloro-2-propyl) phosphate (785 ng L^{-1}) and tris(1,3-dichloro-2-propyl) phosphate (2900 ng L^{-1}) were determined in coastal urban rivers (USA), as well as the synthetic musk fragrance galaxolide (2750 ng L^{-1}) [165]. The organochlorine pesticide metoxychlor (770–11704 ng L^{-1}) was also quantified in a study performed in Karun River, Iran [156]. Molinate was found (up to 2297 ng L^{-1}) in a study performed in rivers and lakes of northern Greece [98]. Iprodione (up to 27140 ng L^{-1}) and clomazone (up to 4400 ng L^{-1}) were determined in some draw wells in Brazil [128]. Phthalate esters were determined (up to 20 μg L^{-1}) in Pearl River Delta, China [146]. Di-n-butyl phthalate was determined in 98% of the samples analysed in China (up to 1520 ng L^{-1}) [136]. The UV filter benzophenone and octocrylene were respectively determined in 95% (up to 5429 ng L^{-1}) and 100% (26–6812 ng L^{-1}) of the samples analysed in Hong Kong, China [62].

Considering the numerous reports herein reviewed on the occurrence of some micropollutants found repeatedly at high concentrations (e.g., pharmaceuticals and pesticides abovementioned, estriol (E3) up to 45500 ng L^{-1} [203] and Bisphenol A up to 4130 ng L^{-1} [124]) and since there is a huge concern about their toxicity to ecosystems including human health, information on their spatiotemporal occurrence and the respective RQs is needed.

3. Future challenges

This Section aims to describe the main gaps of knowledge and future challenges for monitoring campaigns, risk assessment, prevention and mitigation, as well as environmental policy.

The occurrence studies performed worldwide, or even considering Europe only, use different sampling and analytical methodologies, with diverse instrumental performances, which would be standardized to allow widespread adequate measurements. Currently, it is difficult to use the monitoring data published so far to decide which new candidate substances must be included in forthcoming proposals for water monitoring, due to the lack of equivalent criteria [218]. Additionally, the different protocols and criteria adopted for toxicological studies need to be standardized in order to provide a better comparison between different reports [218]. It is known that many of the abovementioned compounds may pose a risk to both human health and ecosystems [207]. When more than one value for a toxicity indicator is available, the lowest value is chosen in order to consider ecological threat for worst-case scenarios. For instance, octylphenol was found up to 542 ng L^{-1} and classified as low risky (<0.1) [18], whereas sulfamethoxazole found up to 56.9 ng L^{-1} was categorized as medium risky (0.1–1) [185] and erythromycin and ciprofloxacin, found up to 126 ng L^{-1} and 33.6 ng L^{-1}, respectively, were classified as high risky (>1) [59]. In the reports herein reviewed, risk assessment was only performed for some organic compounds, such as herbicides [125], hormones [57,58], nonylphenol [18], PAHs [56,146,149], PCBs [74], pesticides [19,105,108,118,119,138], pharmaceuticals (mostly antibiotics) [46,53,59,81,185,188,190,200], phthalates [134,146], POPs [159] and UV filters [62]. Therefore, there is a lack of risk assessment studies and toxicity data for many other compounds [172]. Although data on occurrence is crucial for a deep knowledge about the chemical status of water bodies, the estimation of RQs based on the PNEC values of each substance is decisive for the prioritization process of new EU candidate substances. Besides the analytical limitations and the non-standardized protocols for ecotoxicological studies, some important issues should be also addressed in the future monitoring campaigns, such as determining the precursors of some pollutants, their metabolites and/or their transformation products. Accessing statistically significant data and evaluating mixture adverse effects when determining the RQs, must be also performed. Spatiotemporal occurrence of micropollutants must be statistically evaluated and the reports on this subject should provide additional data for the determined micropollutants, namely the mean and median, in order to better compare studies performed in different locations and/or at different periods.

Concerning the prevention and mitigation, many reviews [6,13,219] have been focusing the need of improving the performance of UWWTPs to remove such type of organic micropollutants, by upgrading the UWWTPs, most commonly employing tertiary treatment processes. Release of organic substances from industries (point sources) and agriculture runoff (diffuse sources) is other issue of high concern. Attempts to reduce the use of toxic compounds or to replace them by other less toxic substances are also needed in both industrial and agricultural activities.

4. Conclusions

The publications herein reviewed show the wide distribution of several PSs, CECs and other pollutants in surface and ground waters. More harmonized studies are needed to get the real scenario of the status of these aquatic compartments. There are many European countries that have not a single surface water monitoring study in the period 2012 – 2017 (40 countries). Considering recent EU Directives, it is extremely important to find out the current situation of these waters. Moreover, the deep knowledge about contamination of surface and ground waters at a global level is important to address efforts needed to prevent the occurrence of relevant organic micropollutants in the environment. Acting on pollutant discharges and controlling the main sources of pollution, as well as developing new wastewater treatment options, are the primary solutions in order to prevent further damage to the environment.

This review shows that the PSs were determined worldwide in the following decreasing order of concentrations: PAHs > atrazine > di(2-ethylhexyl)phthalate > alachlor > hexachlorocyclohexane > trifluralin > heptachlor > trichloromethane > pentachlorophenol > cypermethrin > nonylphenol > naphthalene > diuron > endosulfan > fluoranthene > terbutryn > anthracene > HBCD > dieldrin > aldrin > simazine > dichlorvos, chlorpyrifos > DDT > octylphenol. The other PSs were determined at maximum concen-

trations lower than 0.5 μg L^{-1}. In the case of Watch List compounds, the concentrations were found in the following decreasing order: azithromycin > diclofenac >imidacloprid > EHMC > erythromycin > clarithromycin > EE2 > thiacloprid > clothianidin > acetamiprid > thiamethoxam > oxadiazon > E1 > E2 > methiocarb. Although Directive 2013/39/EU and Decision 2015/495/EU allowed attracting the attention to prevent the adverse effects of specific compounds, many other polar emerging organic compounds have been frequently found, in the following decreasing order of concentrations: caffeine > naproxen > metolachlor > estriol > dimethoate > terbuthylazine > acetaminophen > ibuprofen> > trimethoprim > ciprofloxacin > ketoprofen > atenolol > Bisphenol A > metoprolol > carbofuran > malathion > sulfamethoxazole > carbamazepine > ofloxacin. Monitoring campaigns of the most frequent compounds found at highest concentrations and their risk assessment should be performed in different countries, different seasons, comprising relevant sampling points in a more concerted way.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jhazmat.2017.09.058.

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