Environment International 71 (2014) 46–62

Contents lists available at ScienceDirect

Environment International

journal homepage: www.elsevier.com/locate/envint

Review

Emerging contaminants of public health significance as water quality indicator compounds in the urban water cycle

Amrita Pal [a], Yiliang He [b], Martin Jekel [d], Martin Reinhard [a], Karina Yew-Hoong Gin [a,c,*]

[a] Department of Civil and Environmental Engineering, National University of Singapore, 1 Engineering Drive 2, E1A 07-03, Singapore 117576, Singapore
[b] School of Environmental Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, China
[c] NUS Environmental Research Institute, National University of Singapore, 5A Engineering Drive 1, #02-01, Singapore 117411, Singapore
[d] Technical University of Berlin, Department of Water Quality Control, Strasse des 17. Juni, 10623 Berlin, Germany

ARTICLE INFO

Article history:
Received 28 January 2014
Accepted 30 May 2014
Available online xxxx

Keywords:
Urban water cycle
Emerging organic contaminants
Pesticides
Water reuse
Health impacts
Review

ABSTRACT

The contamination of the urban water cycle (UWC) with a wide array of emerging organic compounds (EOCs) increases with urbanization and population density. To produce drinking water from the UWC requires close examination of their sources, occurrence, pathways, and health effects and the efficacy of wastewater treatment and natural attenuation processes that may occur in surface water bodies and groundwater. This paper researches in details the structure of the UWC and investigates the routes by which the water cycle is increasingly contaminated with compounds generated from various anthropogenic activities. Along with a thorough survey of chemicals representing compound classes such as hormones, antibiotics, surfactants, endocrine disruptors, human and veterinary pharmaceuticals, X-ray contrast media, pesticides and metabolites, disinfection-by-products, algal toxins and taste-and-odor compounds, this paper provides a comprehensive and holistic review of the occurrence, fate, transport and potential health impact of the emerging organic contaminants of the UWC. This study also illustrates the widespread distribution of the emerging organic contaminants in the different aortas of the ecosystem and focuses on future research needs.

Contents

* Corresponding author at: Department of Civil and Environmental Engineering, National University of Singapore, 1 Engineering Drive 2, E1A 07–03, Singapore 117576.

http://dx.doi.org/10.1016/j.envint.2014.05.025
0160-4120/

1. Introduction

The most significant factors affecting the availability and distribution of water in urban settings are population growth and the migration of rural populations to urban areas, resulting in urban sprawl and the rapidly growing number of mega-cities. Urbanization presents a host of technical, ecological and social challenges, most critical ones being supplying fresh water to cities and disposing wastewater without jeopardizing water resources and the environment. Traditionally, fresh water has been extracted from local surface water or groundwater or imported from distant watersheds, and wastewater has been discharged to downstream surface water bodies or the ocean. However, with growing competition among cities for water resources, importing water from distant watershed has ceased being an option in most cases. As a consequence, water planners are forced to develop new supplies from impaired sources, such as wastewater effluent, effluent bearing rivers, brackish estuaries, and stormwater runoff. Implementing water recovery schemes created the UWC (Fig. 1) in which used water is reused directly after advanced treatment or indirectly after discharge to local surface water bodies or groundwater aquifers and cycling the treated water back into the water supply.

While water quality investigations have traditionally focused on nutrients, bacteria, heavy metals and priority pollutants (compounds with known health effects such as pesticides, industrial chemicals, petroleum hydrocarbons) recent research has revealed the occurrence of hundreds of organic contaminants in wastewater and impacted urban surface waters. These novel contaminants belong to diverse compound classes and are typically detected at concentrations in the range 1 ng/L–1 μg/L although concentrations range up to 100 μg/L in some cases. Their toxicological significance is difficult to assess and generally accepted concentration limits for drinking water and discharge limits for wastewater effluent have not yet been established. Collectively, these compounds are referred to as “Emerging Organic Contaminants” (EOCs). Representative compound classes include hormones, antibiotics, surfactants, endocrine disruptors, human and veterinary pharmaceuticals, X-ray contrast media, pesticides and metabolites, disinfection-by-products, algal toxins and taste-and-odor compounds (Richardson, 2003; Shannon et al., 2008). EOCs comprise recently developed industrial compounds that have been newly introduced to the environment; compounds that have been prevalent for some time but are only now being routinely detected owing to improved detection techniques; and compounds that have been prevalent for a long time but have only recently been shown to have harmful eco-toxicological effects (Houtman, 2010).

Environmental contamination of EOCs has been reviewed from several perspectives, including developments in analytical techniques (Dirtu et al., 2012; Farré et al., 2012; Lepom et al., 2009; Richardson, 2012), occurrence of EOCs in surface waters (Houtman, 2010; Pal et al., 2010; Schriks et al., 2010; Thomaidis et al., 2012), ground water (Jurado et al., 2012; Lapworth et al., 2012), sludge (Clarke and Smith, 2011; Tadeo et al., 2012) and drinking water (Delgado et al., 2012a; Delgado et al., 2012b; Houtman, 2010; Post et al., 2012), and (eco)

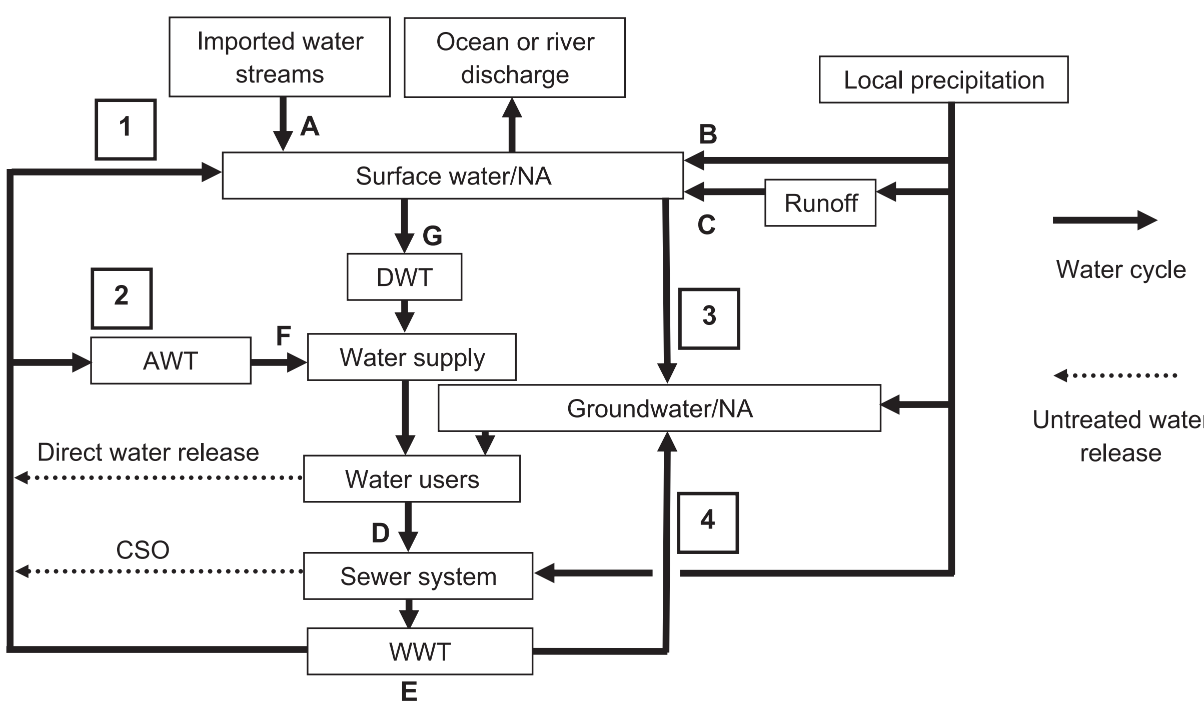

Fig. 1. Schematic of generic urban water cycle: (1) indirect reuse via surface water; (2) direct reuse by advanced wastewater treatment (AWT); (3) recharge of effluent bearing river water (bank-filtration); (4) artificial recharge of aquifers with effluent, referred to as soil-aquifer treatment (SAT). A–F: Entry points of EOCs: A: upstream effluent discharge; B: wet (rainwater) and dry deposition; C: runoff; D: wastewater discharge from sources including domestic, industrial and hospitals, clinics and medical centers; E: treated effluent; F: disinfection by-products produced during AWT; G: *in situ* produced algal toxins and taste and odor compounds.

toxic effect and risk assessment along with regulatory implications (Flint et al., 2012; Hernando et al., 2011; Murphy et al., 2012; Murray et al., 2010; Rodriguez-Moza and Weinberg, 2010; Sapkota et al., 2008; Schriks et al., 2010). This review summarizes data on EOC occurrence in the UWC, assesses potential health risks stemming from exposure to selected contaminants and identifies research needs. The number and diversity of EOCs that have been identified is growing and now exceeds twenty compound classes with each class comprising of hundreds of specific compounds (Houtman, 2010). Because data on UWC flows and EOC occurrence is still fragmented, this review was limited to four cities (Orange County, Singapore, Berlin, and Shanghai) and compounds for which data is relatively complete. The need for this review stems from the difficulty to efficiently assess and mitigate water quality impacts by EOCs and the lack of comprehensive studies that document occurrence, fate, transport and potential health issues of EOCs in the water cycle of large cities. Such information is required to develop management and policy approaches and research programs, specifically to identify and remove sources and sinks, block conduits that feed contaminants into the UWC, identify pathways and sinks where contaminants are destroyed or removed, and to assess potentially adverse effects on humans and ecosystems.

2. The urban water cycle

Fig. 1 is an example of a generic urban water cycle (UWC) which includes direct and indirect reuse of water, recharge and artificial recharge and all possible ways by which contaminants can enter the system and get attenuated along the way. The UWC as shown in Fig. 1 consists of four distinct sub-cycles, all feeding degraded water back into the urban supply: (1) wastewater treatment (WWT) effluent and runoff enter surface water and after treatment are fed into the water supply system (indirect reuse); (2) WWT effluent is treated by advanced wastewater treatment (AWT) processes to meet drinking water standards (for instance by reverse osmosis and advanced oxidation processes) and injected directly into the water supply system (direct reuse), aquifers, or reservoirs; (3) effluent is discharged into surface water from where it is infiltrated into aquifers (bank-filtration) that serve concurrently as storage and distribution systems for potable water (Grünheid et al., 2005; Jekel et al., 2013), and (4) effluent is treated to high standards such that it can be used for aquifer recharge. The latter practice is referred to as soil-aquifer treatment (SAT) (Drewes et al., 2003). With increasing urbanization, the quantities of consumer and health care products that are released into the UWC increases thereby burdening treatment facilities and causing them to accumulate in water supplies. Contaminants enter the UWC in the absence of a sewer system through direct discharge by the user into surface water bodies, release from the sewer, combined sewer overflow (CSO), or discharge from wastewater treatment plants. Not considered here are diffuse or so-called non-point sources. Contaminant removal from the cycles occurs prior to wastewater release at the WWT, during transport in the UWC by natural attenuation (NA), e.g., chemical or biodegradation, adsorption, prior to consumption at the drinking water treatment (DWT), or by discharge to oceans or rivers.

In contrast to flow in the natural water cycle, which is dominated by rain events, flow in the urban UWC is dominated by flows that meet the water supply and wastewater disposal requirements. Typically, water enters the UWC as natural streamflow, as local precipitation, or as imported water. Precipitation that does not infiltrate naturally into local aquifers is either infiltrated artificially or collected as runoff and directed into local surface rivers, lakes, and reservoirs. Stormwater that is collected in the sewer system is discharged into the surface water as CSO. Water discarded by households and commercial users is collected in the sewer system and treated by WWT plants such that it can be discharged into surface waters. Aquifers are sometimes an integral part of the water supply system and can play an important role as both storage and treatment systems. During rainy periods, excess surface water and runoff is percolated into aquifers and withdrawn during dry periods. This practice, referred to as "conjunctive use" increases water reliability, protects water quality, provides treatment. Aquifers are replenished by natural infiltration of surface water or artificially by direct injection or bank-filtration, which involves inducing a negative hydraulic gradient between the surface water surface and the production well. The latter is significant in cities that rely on groundwater for their drinking water supply, such as Berlin (Hass et al., 2012; Heberer et al., 2002). Surface water and groundwater transport can provide natural water purification, often referred to as natural attenuation or, because the performance of natural systems is usually closely monitored, as natural monitored attenuation (NMA). Natural attenuation processes are often highly effective so that the need for DWT is reduced to filtration, aeration, and disinfection, depending on local conditions and regulations.

The generic UWC shown in Fig. 1 is expected to vary from city to city depending on climate, hydraulics, population, political and other factors. There can be various manifestations of the water cycle from city to city and the four scenarios we have discussed below are representative urban water cycles, respective to that particular city/country. Table 1 summarizes characteristics of four UWCs that are representative for rapidly growing and densely ($\geq$3,000/km^2) populated cities in four different climate zones: semi-arid (Orange County), temperate-continental (Berlin), subtropical-monsoon (Shanghai), and tropical-rainforest (Singapore) regions. These cities meet the water needs of their large populations by relying on a highly sophisticated infrastructure that is designed to maximize water use efficiency. A novel concern water planners are confronted with is the occurrence of emerging contaminants in the UWC. The discovery of these contaminants is relatively recent and there is insufficient data to comprehensively assess their significance in the UWC. Each of the following cities/countries has used a well-developed method of tapping water to make clean potable water available for the highly dense urban population.

2.1. Orange County Water District (OCWD)

The OCWD encompasses an urbanized area of 927 km^2 with 2.4 mio people and is situated on the coastal plane of Southern California. The climate is semi-arid with precipitation averaging approximately 0.36 m/y. The UWC of the OCWD is characterized by three major components: surface water with high effluent content, groundwater recharge by advanced treated wastewater, and imported water. The data in Table 1 shows that the OCWD meets the bulk of its water needs by importing water from the Colorado River and the Sacramento/San Joaquin Delta and by capturing nearly quantitatively the flow of the Santa Ana River. Imported water and Santa Ana River flow are percolated into the local groundwater basin for conjunctive use. Nearly the entire flow of the Santa Ana River is supplied by effluent of upstream WWT plants, except during the wet winter months when run-off can be significant. Imported water and river flow are percolated into the carefully managed groundwater basin. Additional water for groundwater recharge is produced by purifying wastewater effluent using advanced wastewater treatment (AWT) (microfiltration, reverse osmosis and advanced oxidation) (OCWD, 2005). Entry points for EOCs are the effluent bearing Santa Ana River in which pharmaceuticals and other EOC were detected (Gross et al., 2004), and AWT product water, which contains traces of the disinfection by-product N-dimethyl-nitrosamine (NDMA) (Plumlee et al., 2008). Some EOCs occurring in the Santa Ana River are attenuated naturally in the river and wetland (Lin et al., 2006) and during infiltration and groundwater transport (Ding et al., 1999).

2.2. Singapore

The city of Singapore with a population of 5.3 mio people is situated on a small tropical island covering an area of 714 km^2. The average

Table 1
Urban water cycle characteristics and approximate flows.

UWC characteristics	Orange County[a]	Singapore[b]	Berlin[c]	Shanghai[d]
Population, mio	2.4	5.3	3.4	23
Area, km^2	927	714	889	6,400
Av. precipitation, m/y	0.36	2.34	0.57	1.59
River inflow into city Av. flow, m^3/s	Santa Ana, 4.2	0	Spree, 13 Havel, 35	Yangtze, 30,000 Huangpu,180
Total water demand, m^3/s (=100%)	16.3	12.7	6.53	165.2
Local runoff, %	N.R.	23	6.0	2.8
Incidental recharge, %	6	0	N.R.	N.R.
Groundwater, %	68	0	100	0.02
Imported water, %	26	23	0	0
Indirect reuse, %	17	30	45	N.R.
Seawater desalination, %	0	≈10	0	0
EOC entry points	Upstream effluent discharge, AWT, runoff	Runoff, leaking sewer water	Effluent discharge into urban rivers	Effluent discharge into surface water
Climate	Semi-arid	Tropical-rainforest	Temperate-continental	Sub-tropical
Hydrogeography	Inflow of effluent fed river	No natural lakes, no aquifers	Low precipitation Inflow of small rivers	Inflow of highly used rivers
Distinct feature of the UWC	Imported water, artificial groundwater recharged with surface water and AWT	Stormwater harvesting, reclaimed water, imported water, artificial reservoirs, desalination	Artificial recharge, bank filtration	Reservoir in estuary for capturing river flow

Note: N.R. – Not Reported.
[a] OCWD information: (OCWD, 2005; OCWD, 2013a; OCWD, 2013b).
[b] Singapore information: (PUB, 2013).
[c] Berlin information:http://www.stadtentwicklung.berlin.de/umwelt/umweltatlas/i110.htm; (Hass et al., 2012; Heberer et al., 2002; Richter et al., 2008).
[d] Shanghai information: (Chen et al., 2009a; Zhang, 2007; Zhou et al., 2011), http://www.shanghaiwater.gov.cn/.

precipitation is 2.34 m/y but the island has no natural lakes and aquifers to store water. Singapore's UWC is characterized by efficient stormwater harvesting, water reuse and desalination with imported water providing the balance. To meet its water needs, Singapore relies on four water sources ("four taps strategy") (PUB, 2013): (1) rain water collected from 2/3 of its land area in 17 artificial reservoirs (23%), (2) water imported from Malaysia (37%), (3) reclaimed water (NEWater) (30%), and desalinated water (10%). (Percentages vary depending on rainfall and other factors). Singapore is aiming to lower dependence on imported water by increasing indirect water reuse and water use efficiency, improving water quality management and lowering production and management costs, and desalination (Tortajada, 2006). There is no direct discharge of effluent into the city's rivers but studies of surface waters from a highly urbanized catchment in Singapore still showed the presence of EOCs, perhaps from leaky sewer systems or from non-point sources (Xu et al., 2011).

2.3. Berlin

Berlin is located in a relatively dry region in North-Eastern Germany (average precipitation 0.57 m/y). The relatively small Spree and the Havel Rivers (average flows 13 and 35 m^2/s, respectively) supply most of Berlin's surface water. These rivers receive relatively high flows of tertiary treated wastewater upstream of the city boundaries. While flowing through the city, these rivers receive the discharge of six conventional WWT plants. The fraction of effluent in Berlin's surface waters is on average 40% and may be as high as 84% (Heberer et al., 2002). The city draws 100% of its drinking water from local aquifers that are recharged artificially (approximately 10%) and by induced bank-filtration (approx. 60%). Because of the tight connection between effluent discharge, bank-filtration and groundwater withdrawal, Berlin's water cycle has been characterized as "semi-closed" (Grünheid et al., 2005; Hass et al., 2012; Richter et al., 2008). As a result, the fraction of water that passes through the cycle at least once is relatively high (45%). EOC concentrations in surface and groundwater concentrations exceed 1 μg/L in some cases (Ternes, 1998). However, the combination of WWT and natural attenuation during river transport, bank-filtration and groundwater transport have been deemed effective at removing EOCs to below acceptable target concentration.

2.4. Shanghai

Shanghai's population of 23 mio (including 9 mio migrants) have been relying on Huangpu (5.67 Mm^3/d) and more recently on the mighty Yangtze River (30,000 Mm^3/d) for water supply. The Huangpu originates in the Dianshan Lake, is about 113 km long, and empties into the estuary of the Yangtze River. The 83 km stretch of the Huangpu that flows through the Shanghai metropolis receives most of the treated and untreated wastewater discharges of the city. The Huangpu River is contaminated with heavy metals, polyaromatic hydrocarbon compounds (PAHs). Reported concentration of contaminants such as perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) (Chen et al., 2009a; Zhang, 2007) and the pharmaceutical carbamazepine (CBZ) (Zhou et al., 2011) in the Huangpu are 20.5, 1590 ng/L (Chen et al., 2009a), and 530 ng/L (Zhou et al., 2011), respectively. These values are higher than that typically reported for urban rivers. To meet the increasing demand and to protect the intake from saline water intrusion during drought periods, Shanghai built the Qingcaosha Reservoir inside the mouth of the Yangtze River. With a capacity of 71.9 Mm^3/d, Qingcaosha Reservoir has now become its primary water supply, meeting the needs of 10 million people. Detailed EOC data has not been reported yet.

3. Sources of emerging contaminants the urban water cycle

The main entry points of EOCs into the UWC are indicated in Fig. 1. EOC sources include households, hospitals, construction, landscaping, transportation, commerce, industrial scale animal feeding operations, dairy farms, and manufacturing. Additional sources include leaking sewer lines, landfills and inappropriately disposed wastes. In some cases the inflow consists of a high fraction of effluent from upstream communities [A], as is the case for the Santa Ana River in OCWD. River transport, flow through wetlands, and groundwater recharge and transport can attenuate EOC concentrations to below the detection limit by natural attenuation processes such as dilution, sorption, volatilization, and degradation (Gross et al., 2004; Grünheid et al., 2005; Lin et al., 2006). Both rain and runoff, [B] and [C], respectively have been identified as sources for EOCs. For example, perfluorinated compounds (PFCs) (Nguyen et al., 2011), polycyclic aromatic hydrocarbons, polychlorinated biphenyls, methyl tert-butylether (Sablayrolles et al., 2011), nonylphenols and nonylphenol ethoxylates (Xu et al., 2011) have been reported to be present in rainwater. Urban and suburban surfaces (roofs, pavements, roads and parking lots) prevent infiltration of precipitation, rapidly channeling water into streams, rivers and reservoirs. Precipitation leaches toxic chemicals from building, street and land surfaces or improperly disposed wastes and transports them into surface waters, potentially degrading water resources and harming ecosystem health (Xu et al., 2011). Moreover, heavy rainfall eventually leading to flash floods can erode sediments on landfills and agricultural fields, leading to the possible release of organic pollutants, including pesticides (Moreno-González et al., 2013), into surface waters. Also during the rainy season, a surge in the loadings of indicator chemicals such as caffeine in surface waters due to CSO has been documented (Buerge et al., 2006). A recent study on PFCs shows higher concentrations of PFCs in storm runoff than dry weather flow, suggesting a 'first flush' effect which could be due to the leaching of suspended solids containing PFCs by the storm water from non-point sources present in the urban catchment (Nguyen et al., 2012).

EOCs enter the UWC mainly via the sewer system and if removal by WWT plants is incomplete, they are discharged into the receiving surface water bodies (Daneshvar et al., 2012), [C]. EOCs are released into water bodies receiving effluent [D]. Discharge of CSO in well-developed water infrastructure systems is estimated to be 1–5% of wastewater treatment plant (WWTP) flow. Impacts can be significant at sites where direct wastewater, leakage from sewers, or CSO enter water bodies that are used as raw water supply. EOC sources are too numerous to be specifically indicated in Fig. 1. Major ones include, for example, leaky sewer systems (Christensen, 1998), landfills (Chen et al., 2010a; Kümmerer, 2009), chemical storage facilities (Lapworth et al., 2012), fire fighting training sites (Moody and Field, 1999; Nguyen et al., 2011), feed lots of animal feeding operations (Brown et al., 2006), and runoff from industrial sites (Lin et al., 2010a). For many EOCs sources and pathways remain to be identified.

4. Classes of EOCs occurring in the urban water cycle

Although new EOCs continue to be discovered, this review is focused on the sixteen EOC groups listed in Table 2a, which lists compound categories, representative chemicals, production capacities, activities that cause their release into the UWC, and estimated quantities that are released to water bodies. EOCs are entering the UWC from a variety of sources and as a consequence of numerous activities, including sewage discharge, compounds leached from landfills, leaking chemical storage facilities, construction sites, inappropriately disposed wastes, street pavements, painted facades, tar roofs, and leaking sewers. Other EOCs are formed *in situ* during transport in the water cycle or during treatment: for instance, algal toxins and taste-and-odor compounds are formed in eutrophic reservoirs, and metabolites and disinfection by-products can be formed during treatment. Here we focus on the sixteen representative compounds of the most commonly detected EOCs classes. These EOCs can serve as "indicator compounds" because they are of potential human health and ecotoxicological significance and cover a broad spectrum of compound properties, structures, and environmental behaviors. Because they are readily detected using state-of-the-art equipment, numerous laboratories have reported data on their occurrence. In terms of chemical properties, EOCs include hydrophobic (flame retardants, estrone), surface active (PFOS, 4-nonylphenol monoethoxylate), high molecular (microcystin, iopromide), polar (sucralose), volatile (geosmin) compounds. Focusing monitoring programs on a limited number of indicator compounds might make it easier in the future to compare contaminant occurrence and behavior in different water cycles.

4.1. Plasticizers

Plasticizers comprise of alkylesters (o-phthalic acid), naphthalene sulfonates, and a variety of other compounds that are added to materials such as plastics, concrete, clays, and gypsum to improve plasticity and rheological properties. Some plasticizers are potential endocrine disruptors. BPA, for example, a component of polycarbonate plastics, has been used in diverse applications ranging from food and beverage containers, flame retardants, adhesives, building materials, electronic components, eyeglass lenses, dental sealants to paper coatings (Bang et al., 2012; Vandenberg et al., 2007). With a yearly global production of 11.5 billion pounds or 5,216,312.3 t in 2008 (Dow, 2012), BPA is one of the highest produced chemicals in the world and typifies our growing dependency on synthetic chemicals. BPA enters the water cycle through several different pathways including plastic manufacturing plants, during the natural breakdown of plastics, exhaust from domestic waste incinerators, leachates from landfills and discharge of WWTP effluents. As summarized in Table 2a, the total global release of BPA in 2007 was 1,132,062 pounds or 513.5 t, out of which 6,246 pounds or 2.8 t was directly released to water (USEPA, 2010).

4.2. Perfluorinated surfactants

Similar to BPA, PFCs have been used in a wide variety of commercial products (surfactants, emulsifiers, wetting agents, additives, aviation hydraulic fluids, fire-fighting foams, paints, adhesives, waxes, polishes, and water-, soil- and stain-resistant coatings for clothing, leather, upholstery, and carpets and oil-resistant coatings for cooking pans) for over 60 years (Post et al., 2012). PFCs enter the UWC mainly through discharges from manufacturing industries and effluents from WWTPs, resulting in surface water concentrations in the order of tens to hundreds of ng/l. PFCs occur as complex mixtures with PFOS and PFOA typically being the major components. Removal of these PFCs in WWTPs is incomplete. If biotransformation occurs at all, only the non-perfluorinated portion of the PFC compounds is affected, causing WWTPs to discharge increased levels of refractory metabolites, predominantly PFOA and PFOS (Lin et al., 2010a). It is important to note here that occurrence studies on the detected levels of PFOS and PFOA in human umbilical cords have proved that these PFCs could cross the human placenta (Apelberg et al., 2007). According to a survey on the production and release of PFCs, $<$2.5 t of PFOS or PFOS-related substances were released during 2008 out of which around 1.25 t was released on-site to waterways (Table 2a) (OECD, 2011).

4.3. Pesticides

The use of pesticides in agriculture and forestry, horticulture, or amenities which include highways, airports, railways, industrial sites, parks, golf courses, public spaces, and other sports grounds, also increases with urbanization (Hernando et al., 2011). When applied to crops for their protection against different pests and diseases, pesticides eventually reach the soil by being washed rain or irrigation water or by spray drift (i.e., the wind-induced untargeted movement of the pesticide droplets or residues). From the soil, the pesticides (such as terbuthylazine, chlorpyrifos and atrazine) drift to aquatic environments including ground waters and surface waters (Moreno-González et al., 2013).

4.4. Surfactants

Alkylphenolethoxylates (APEOs) are non-ionic surfactants widely used in the formulation of a large variety of detergents, paints, resins, pesticides and lubricants. Alkylphenols such as 4-nonylphenol (NP) and 4-tert-octylphenol (OP) are biotransformation products of their corresponding APEOs. Nearly 80% of global production of APEOs comprise of nonylphenolethoxylates (NPEs), widely used for making pesticides, in the form of wetting agents or as dispersants or emulsifiers, and it has been reported that 37% of NPEs are released undegraded to the water (Linley-Adams, 1999).

Table 2a
Categories, sources, annual production and releases of representative EOCs and activities causing release into the UWC.

Categories	Representative chemicals			
	Chemicals	Annual production capacity, year*, ref.	Activities causing contaminant release to UWCs	Annual release to water, year*, ref.
Plasticizers	Bisphenol A	5,216,312.3 t (global), 2008, (Dow, 2012)	Plastic manufacture from plants; combustion of domestic waste; natural breakdown of plastics in environment; landfill leachates; WWTP effluents	2.8 t, (global), 2007, (USEPA, 2010)
Perfluorinated compounds	PFOS	73–162 t (global), 2005, (OECD, 2006)	Manufacturing wastes; via volatilization, oxidation & precipitation from pesticides, PCPs, flame retardants, upholstery, coatings, food-packaging etc.; landfill leachates; WWTP effluents	<1.25 t (global), 2008, (OECD, 2011)
Pesticides	Fipronil	480 t (France), 1997, (Tingle et al., 2000)	Spray drift after various applications: pest control & crop protection, irrigation runoff	-
Surfactants	4-nonylphenol monoethoxylate (NP1EO)	118,000 t nonylphenolethoxylates (Europe), 1997, (Wenzel et al., 2004)	Application of raw sludge to soils followed by landfill leachates; WWTP effluents	~37% released to water undegraded, (Linley-Adams, 1999)
Antibiotics	Sulfamethoxazole	53.6 t[#] (Germany), 2001, (Huschek et al., 2004); 10.9 t[a](Spain), 2009, (Ortiz de García et al., 2013)	Manufacturing wastes; domestic and farm disposal of unused, expired antibiotics; land use of animal manure and sewage sludge; WWTP effluents	2.1 t[b] (Spain), 2009, (Ortiz de García et al., 2013)
Pharmaceuticals	Acetaminophen	621.6 t[#] (Germany), 2001, (Huschek et al., 2004); 1,460.2 t[a] (Spain), 2009, (Ortiz de García et al., 2013)	Manufacturing wastes; unused and expired drugs disposed from households; landfill leachates; WWTP effluents	23.3 t[b] (Spain), 2009, (Ortiz de García et al., 2013)
Hormones	Estrone (E1)	-	Hormones injected to livestock and fishes, released from animal farms and aquacultures respectively; human and animal excreta via WWTP effluents	28.2. kg[b] E1 metabolite, (Spain), 2009, (Ortiz de García et al., 2013)
Iodinated X-ray contrast media (ICM)	Iopromide	64.1 t[#] (Germany), 2001, (Huschek et al., 2004); 23.7 t[a] (Spain), 2009, (Ortiz de García et al., 2013)	Manufacturing waste; excreted from human bodies after intravascular administration at hospitals and released via WWTP effluents	14.8 t[b] (Spain), 2009, (Ortiz de García et al., 2013)
Artificial sweeteners	Sucralose (SCL)	15,000 t (global), expected by 2018 (Searby, 2011)	Direct release from food industries, households, animal farming; WWTP effluents as excretion after consumption without undergoing change within the human bodies	98% of SCL consumed by humans excreted unchanged, (Loos et al., 2009)
Musks& fragrances	Galaxolide	1000–5000 t (Europe), 2004, (Fernandes et al., 2013)	Applied as perfumes, cosmetics, soaps, lotions and washed by water; WWTP effluents	~77% used musks drains into sewage, (Fernandes et al., 2013)
UV-filters	4-methylbenzylidene camphor (4-MBC)	10,000 t UV-filters (global), (Gago-Ferrero et al., 2012)	Use of sunscreens, shampoos, whitening lotions, cosmetics, lipsticks, hairsprays & dyes: released through swimming and showers	-
Antimicrobial preservatives	Benzylparaben	<7.7 t total parabens, (USA), (Dobbins et al., 2009)	Manufacturing wastes; runoffs through use in cosmetics, toiletries, pharmaceuticals, food; WWTP effluents	2.1 t[b] methylparaben (Spain), 2009, (Ortiz de García et al., 2013)
Other personal care products	N,N-diethyl-m-toluamide (DEET)	1,814.4 t[c], (USA), 1990, (USEPA, 1998)	Mosquito repellants: released through showers, swimming as <20% absorbed dermally; WWTP effluents	>80% released to water, (Aronson et al., 2012)
Fluorescent whitening agents (FWAs)	4,4′-bis(2-sulfostyryl) biphenyl (DSBP)	3,000 t estimated (global), 1992, (Kramer et al., 1996)	Used in laundry detergents: 5–80% remain in washing liquor and are disposed to sewers	5–80% discharged with wash liquor, (Kramer et al., 1996)
Algal toxins	Microcystin	-	Many species of cyanobacteria produce toxins in water impacted by algal blooms	-
Off flavors	Geosmin	-	produced by: algal blooms, & natural bacterial populations such as actinobacteria	-

* The year has been included where data was available.
[#] Annual sales.
[a] Estimation of pharmaceutical active compound consumption.
[b] Occurrence in aquatic environment.
[c] Average annual estimate of domestic usage of DEET (active ingredient).

4.5. Pharmaceuticals

The release of pharmaceuticals and their human metabolites into waterways is of increasing concern. Pharmaceuticals are found in the environment as parent compounds or as metabolites or conjugates, mainly because of disposal to the sewage system. They are relatively polar, multifunctional and incompletely removed by WWTPs. In many cases, effluents containing pharmaceuticals from hospitals/clinics/medical centers that are directly released to the nearby river waters and not collected by sewer system may be a significant contaminant source to environmental waterways (Lin et al., 2010b). As illustrated in Table 2a, out of the 10.9 t of the estimated antibiotic sulfamethoxazole consumption in Spain in 2009, 2.1 t had been found to occur in the aquatic environment, while 23.3 t out of 1,460.2 t of the analgesic acetaminophen was found to occur in water, in the same study (Ortiz de García et al., 2013). This could be due to elimination from urban WWTPs. Urban WWTPs, for example, have been identified as a major source of antibiotics (Michael et al., 2013). A growing environmental concern is antimicrobial resistance, which primarily arises from increasing levels of residual antibiotics lingering in environmental water and soils. Antibiotic resistant genes can be transferred to pathogenic bacteria to subsequently infect human beings with potentially devastating consequences (Kim and Aga, 2007). Cross resistance has been known to occur, whereby resistance developed by a bacterial strain against a certain class of antibiotics could apply to other classes of antibiotics as well (Kümmerer, 2009). A mixture of different classes of antibiotics are constantly added to the UWC as antibiotics are not only widely used in households and hospitals but also commonly used for animal farming, veterinary and agricultural use. Another study has reported that sulfamethoxazole is not degraded in sewage treatment plants (Park and Choi, 2008). This problem of antimicrobial resistance could prove to be a major challenge in years to come. Apart from antibiotics, other environmental pharmaceuticals most often include painkillers, antihistamines, β-blockers, lipid regulators, anti-depressants, antiepileptics, antidiabetics, analgesics and anti-inflammatory drugs, birth control pills, blood thinning agents, and anti-itch and anti-fungal drugs. Anti-cancer drugs, also known as antineoplastics and cytostatics, are cytotoxic, genotoxic, mutagenic or teratogenic (Kosjek and Heath, 2011). Natural and artificial hormones, another group of EOCs, are also constantly added to the aquatic environment through human and animal excreta via WWTP effluents.

4.6. Personal care products (PCPs)

PCPs include mosquito repellants, antimicrobial and antifungal agents, surfactants, perfumes and sunscreens which are widely used and form a permanent feature of urban lifestyles. Personal care products, unlike pharmaceuticals, are applied externally and hence do not undergo any metabolic changes prior to their release to the aquatic environment. However, being extensively used on a day-to-day basis, they are also highly detected in surface waters and have the potential of bioaccumulation (Brausch and Rand, 2011). For example, only less than 20% of N,N-diethyl-m-toluamide (DEET), the active ingredient in mosquito repellants is absorbed through screen while over 80% of the remaining is released to water (Aronson et al., 2012). The polycyclic musk galaxolide is a common ingredient of fragrances. In 2004, between 1,000–5,000 t of this chemical was produced in Europe alone. It has been estimated that 77% of the used musks were drained in the sewers (Fernandes et al., 2013).

4.7. Fluorescent whitening agents (FWAs)

FWAs are highly conjugated fluorescent compounds that are added to textiles, laundry detergents, and paper and plastic products, mostly to enhance white color. FWA enter surface waters via wastewater discharges (Hayakawa et al., 2007). Many FWAs are relatively water-soluble, non-biodegradable and therefore, used as markers for wastewater in surface waters (Managaki et al., 2006). It has been reported that 5–80% of 4,4′-bis(2-sulfostyryl) biphenyl (DSBP), an FWA generally used for detergents and papers, is released with the wash liquor to the aquatic environment (Kramer et al., 1996).

4.8. X-ray contrast media

The X-ray contrast media are injected intravascularly at high doses to enhance the contrast of X-ray images of organs and blood vessels. They are metabolically stable and usually excreted within a day of intake. The contrast media detected in urban waters include iopamidol, iopromide and iohexol, which are very persistent and polar in nature (Drewes et al., 2001). The removal of iodinated X-ray contrast media (ICM) in conventional biological wastewater treatment is limited and among the commonly used ICMs, only iopromide is degraded by around 60–70%. These ICMs have been found to occur in surface waters and ground waters at μg/l concentrations (Pérez and Barceló, 2007; Weissbrodt et al., 2009). As listed in Table 2a, out of the 23.7 t of estimated annually produced iopromide in Spain in 2009, around 14.8 t were released in water (Ortiz de García et al., 2013).

4.9. Artificial sweeteners

Consumption of artificial sweeteners has become a lifestyle habit as these are low calorie products. Unlike sugar, these compounds do not cause an insulin response and can be consumed by diabetics. They are also not fermented by microbes that cause dental plaques. These chemicals are ubiquitous in surface waters and include saccharin, cyclamate, aspartame and sucralose. Ever since the introduction of sucralose in 1998, these and other artificial sweeteners have been increasingly used in the developed countries. The annual productions of aspartame and sucralose in the US are 16,000 t and 1,500 t respectively. Aspartame, for example, is used in more than 6,000 products in the US (Kokotou et al., 2012). Around 98% of the sucralose consumed by humans is excreted without undergoing any change and with a half life of several years, it can be very persistent in the aquatic environment (Loos et al., 2009).

4.10. Flame retardants

Flame retardants like polybrominated diphenyl ethers (PBDEs) are another group of EOCs indispensible to the urban world as they are widely used in thermostats, textiles, thermoplastics, coatings in furniture and electronics to prevent the spread of fires. Due to their hydrophobic nature, these compounds are found at higher concentrations in sediments than in surface waters (Schriks et al., 2010). However, they can usually be easily transported long distances away from their source of release and studies have shown their regular presence in human and animal tissues, blood and milk (Ela et al., 2011; Houtman, 2010).

4.11. Algal toxins and off-flavor compounds (OFCs)

Algal toxins and OFCs can be formed *in situ* in eutrophic lakes and reservoirs, often due to the presence of excess nutrients and agricultural wastes (Davidson et al., 2012). In freshwaters, many species of cyanobacteria produce toxins which can enter the UWC through waters impacted by algal blooms. These cyanotoxins can harm humans and animals, and include microcystins and nodularins (hepatotoxins), cylindrospermopsins (affect the liver and kidneys) and anatoxins and saxitoxins (neurotoxins) (Delgado et al., 2012a).

Microcystin for example has been shown to accumulate in digestive glands of freshwater clams. Thus clams exposed to cyanobacterial blooms could potentially accumulate large quantities of microcystin and adversely affect mammals and birds feeding on them and thus indirectly affect humans (Sabatini et al., 2011). Algal blooms, in addition to natural bacterial populations (Actinobacteria), also produce off flavor compounds (OFCs). Two of the more common OFCs are geosmin and methyl isoborneol (MIB), which have a distinct earthy-muddy flavor, and are mostly produced by cyanobacteria although heterotrophs (actinomycetes, e.g., *Nocardia* and *Arthrobacter*), fungi and other microorganisms have also been identified as the source of OFCs (Jüttner and Watson, 2007). In spite of the many published studies on geosmin and MIB, the exact reaction mechanism producing them and many of their biological sources are still unknown. Research shows that light, nutrients, temperature, and the presence of microorganisms effect formation and the release of the protein bound and intracellular OFCs into the surface water (Jüttner and Watson, 2007; Parinet et al., 2010).

4.12. Disinfection by-products (DBPs)

DBPs such as brominated, chlorinated, iodinated or nitrogen containing disinfection by-products can enter the drinking water supply via water purification processes and are formed during the reactions between disinfectants and natural or man-made organic matter present in water (Wu et al., 2010). Some of the newly emerging DBPs are formed in chlorinated or chloraminated water and have carcinogenic potential. These include nitrosodimethylamines (NDMA), iodo-acids, iodo-trihalomethanes, bromonitromethanes, haloamides and haloaldehydes.

4.13. Benzothiazoles and benzotriazoles

Benzothiazoles are another group of EOCs that frequently occur in UWCs (Kloepfer et al., 2004, 2005). Benzothiazole derivatives occur as 2-mercapto-, 2-hydroxy-, 2-sulfonic acid-, 2-methyl-, benzothiazoles and have wide applications as fungicides, herbicides, accelerators for vulcanization of rubber, biocorrosion inhibitors, and also in dye production and lumbar and leather productions (Kloepfer et al., 2004). These are often detected in river waters and most importantly their occurrence could also be indicative of street runoff because of their use in rubber and tire manufacturing industries (Pan et al., 2012; Reemtsma et al., 1995). Similarly, different modifications of corrosion inhibitor benzotriazole are frequently found at μg/L concentration (Reemtsma et al., 2010; Voutsa et al., 2006). Because benzotriazole is relatively refractory, it can serve as a conservative tracer.

Potential risks of these chemicals to humans and terrestrial and marine animals are summarized in Table 2b. Tables 2a and 2b complement each other: depending on the extent of adverse effects of a representative chemical on the ecosystem, its release to the UWC needs to be regulated or if a chemical is discharged to the water in high amount, further research needs to be carried out on its impact to the ecosystem. As illustrated in Table 2b, for example, PFOS, microcystin, fipronil and BPA, have shown the possibility of having carcinogenic effect on humans (Lindstrom et al., 2011; Sedan et al., 2013; Tingle et al., 2000; Wu et al., 2012). Since BPA has potential endocrine disruptive effects on humans, animals, birds and has shown estrogenic and reproductive effect on marine organisms (Flint et al., 2012), its release to the UWC needs to be monitored and regulated. From the thorough review of the potential adverse effects of the chemicals (Table 2b), it can be concluded that although most chemicals are either endocrine disruptive, carcinogenic, estrogenic or in any other way toxic to humans, the concentrations at which they are harmful are usually much higher than that found in the aquatic environment. Nevertheless, Table 2b also illustrates that most of the chemicals could still possibly affect ecosystem (such as bees, birds, worms, fishes, mussels, plants, animals) and thus indirectly affect humans in the long run. Although chemicals such as sucralose illustrated in Table 2b may not have proven significant adverse health effect, they may nevertheless play an important role as a water quality indicator, owing to their ubiquitous presence in the aquatic environment. An important characteristic of a wastewater indicator is that it should not be easily degraded by biological treatment processes at the WWTPs and studies have shown that the biodegradation of sucralose through WWTPs is very low (Oppenheimer et al., 2011).

5. Occurrence of EOCs in urban surface waters

As discussed previously, EOCs originate from various sources (including industries, households, hospitals, animal husbandries, aquaculture, agricultural farms and landfills) and enter surface waters via a wide range of point and non point sources. In our earlier review paper (Pal et al., 2010), we summarized the concentrations of pharmaceuticals and hormones reported in studies between 2006–2009, and showed their decreasing trend in concentration in surface waters due to natural attenuation. Here, we review recent findings on more EOCs in addition to pharmaceuticals and hormones, including plasticizers, stilbenes, surfactants, pesticides and personal care products. These are tabulated with their respective concentrations in surface waters in Table 3. Summarized in Table 3 is the concentration range of emerging organic chemicals occurring in urban surface waters reported in literature between 2005–2013 in different countries and regions like China, Japan, Singapore, Taiwan, USA, Switzerland and Germany. This table surveys the occurrence studies which have been carried out in the different surface waters such as the Pearl river and tributaries, Dianchi Lake, Haihe River and Taihu Lake in China; the Tamagawa and Tone rivers and urban streams in Osaka; the Marina catchment in Singapore; Kaoping river in Taiwan; Glatt and Rhine rivers flowing across Switzerland and Germany; and Mississippi and Hudson rivers in USA.

The median concentrations of BPA reported in 3 different studies in China are 132, 553.3 and 130.3 ng/l respectively (Wang et al., 2012a, 2012b; Yu et al., 2011), close to that of 161 ng/l reported in Singapore's Marina catchment (Xu et al., 2011). Also the maximum concentrations of BPA occurring in China have been found to be 1030 ng/l (Wang et al., 2012b) and 1415.3 ng/l (Yu et al., 2011) while that of 4,230 ng/l in Taiwan (Chen et al., 2010a) is also quite high. However, unlike these Asian countries, Japan has reported a mean concentration of BPA at 27 $\pm$ 19 ng/l (Nakada et al., 2004), similar to the concentration range found in Glatt river of 9–76 ng/l (Voutsa et al., 2006). The occurrence range in Mississippi river in USA is also quite low at 0–147.2 ng/l (Zhang et al., 2007). For PFOS, the concentration levels in all the countries surveyed here are comparable, ranging from 3–25 ng/l (Nakayama et al., 2010; Nguyen et al., 2011). For the insecticide fipronil, occurrence data in surface waters is lacking in countries like China, Japan, Taiwan, Switzerland and Germany and data in Singapore and USA are comparable in nature. Although fipronil has been registered for use against targeted insects to protect crops such as sugarcane and corn, studies have shown that it is detrimental to non-targeted insects, most importantly to pollinators such as bees, rendering it as potentially unsafe to the environment (Jacob et al., 2013). Hence it is important to conduct occurrence studies for fipronil especially in those countries where it is widely used as a common pesticide. For UV-filters such as 4-methylbenzylidene camphor (4-MBC) and antimicrobial preservatives such as benzylparaben, occurrence data in surface waters is lacking in Singapore, Taiwan and USA while data on fluorescent whitening agents are also lacking in China, Singapore and USA (Table 3). An overall survey of Table 3 shows that the concentration levels of most of the EOCs such as BPA, PFOS, sulfamethoxazole, acetaminophen, 4-MBC, galaxolide, benzylparaben and DEET, in Japan, are low compared to other countries.

In general, the occurrence patterns of EOCs would also depend on the extent to which they are naturally attenuated as well as on their removal efficiency in WWTPs (Comeau et al., 2008). For example as reported by Gross et al. (Gross et al., 2004), shallow and unlined rivers could play a significant role in the natural attenuation of contaminants along with adsorption by sediments and photochemical degradation. Ibuprofen, a commonly used non-steroidal anti-inflammatory drug with an annual worldwide production of several kilotons, is not completely removed by the conventional biological waste water treatment plants (Zheng et al., 2011) even though several investigations have shown ibuprofen is susceptible to aerobic biodegradation, e.g., (Kunkel and Radke, 2008; Lin et al., 2006; Yamamoto et al., 2009). Also, EOCs constitute a wide range of chemicals and based on the regulations of individual countries and the degree of usage of the respective chemicals, their release to the environment also varies extensively. For example, in the case of pharmaceuticals, over-the-counter drugs, such as naproxen and ibuprofen are frequently detected in surface waters of countries like Australia (Al-Rifai et al., 2007), Tokyo (Nakada et al., 2008), Singapore (Xu et al., 2011), Turkey (Aydin and Talinli, 2013), Canada (Comeau et al., 2008) and USA (Zhang et al., 2007), as opposed to prescription drugs such as antibiotics. Other factors which could vary the concentrations of the contaminants include rainfall pattern and dilution from mixing with sea water. For example, in an occurrence study on pharmaceuticals and personal care products in surface waters of the Pearl River at Guangzhou, a remarkable difference in detection frequencies and median concentrations of the target compounds was observed during low-flow and high-flow seasons, being much lower in the high-flow seasons, potentially due to the dilution of the contaminants caused by heavy rainfall (Peng et al., 2008). In another study on the occurrence of fluorescent whitening agents across multiple layers of the Tokyo Bay water, a decrease in the concentration of the target compounds was observed with increase in salinity suggesting that the mixing affect of seawater with freshwater, caused a dilution of the contaminants (Managaki et al., 2006).

In Table 3, the water quality guidelines and predicted minimum no-effect concentration (PNEC) values are summarized. The PNEC is defined as the concentration below which unacceptable or harmful effects on organisms are unlikely to occur (Balk and Ford, 1999). In order to calculate the PNEC, the lowest concentration without observed effects (NOEC) obtained in a chronic toxicity test is divided by a safety factor of approximately 100, to account for inter- and intra-species variability (Steger-Hartmann et al., 1999). The respective drinking water

Table 2b
Release of EOCs in the UWC and their potential ecotoxicological effect.

Categories	Representative chemicals	Potential health concerns of representative chemicals				Ref.
		Humans	Animals	Aquatic species	Others	
Plasticizers	Bisphenol A	Possible carcinogenic effect, EDC	Meiotic aneuploidy, synaptic abnormalities, EDC	Estrogenic& reproductive effect	Possible EDC in birds	(Flint et al., 2012; Sharma et al., 2009; Wu et al., 2012)
Perfluorinated compounds	PFOS	Possibility of thyroid disease and low sperm count;	Reduced body weight and cholesterol, increased liver weight, neonatal mortality; carcinogenic to rodents	Mussel mortality observed	-	(Giesy et al., 2010; Lau et al., 2007; Lindstrom et al., 2011; Post et al., 2012)
Pesticides	Fipronil	May pose mild temporary health effect; possible carcinogen but no data so far	Increases thyroid tumors in rats by increasing plasma concentrations of thyroid stimulating hormones	Potential adverse effect on endocrine and neuromuscular systems of larval fish	Highly toxic to lizard, bees (LD50: 0.004 μg/bee), gallinaceous birds	(Beggel et al., 2012; Herin et al., 2011; Lee et al., 2010; Tingle et al., 2003)
Surfactants	NP1EO	Possible endocrine disruptive effect	Possible cardiotoxicty in dogs; possible endocrine disruptive effect	Weakly estrogenic to rainbow trout; weakly toxic to fathead minnow	NPEO mixture weakly toxic to earthworms, plants	(Ademollo et al., 2008; Chen et al., 2009b; Domene et al., 2009; Dussault et al., 2005; Montgomery-Brown & Reinhard, 2003; TenEyck & Markee, 2007)
Antibiotics	Sulfamethoxazole	Mixture with 12 other pharmaceuticals could potentially inhibit the growth of human embryonic kidney cells at ng/l	-	Mutagenic; acute, chronic toxicity at low mg/l; chronic effect on freshwater microalgae *P. subcapitata;* acute effect on cyanobacterium *S. leopoliensis*	Antimicrobial resistance	(Bound et al., 2006; Pomati et al., 2006; Zhang et al., 2010; Zheng et al., 2012)
Pharmaceuticals	Acetaminophen	Alters steroidogenic pathway, increases estrogenicity in adrenal cell H295R high above aquatic concentrations	Chronic hepatoxicity (cirrhosis and hepatocyte necrosis) in mice at high ppm levels	Affects embryonic development of zebrafish; survival of *Daphnia* and fish (Oryziaslatipes) affected at ppm levels	-	(Blanset et al., 2007; Galus et al., 2013; Kim et al., 2012)
Hormones	Estrone	-	-	Fathead minnows: abnormal testicular growth in male at low ng/l; chronic exposure causes feminization	Potato plant, sunflower seedlings: affect flowering, root, shoot growth with E2	(Hamid & Eskicioglu, 2012; Hanselman et al., 2003)
ICM	Iopromide	Possibility of low human toxicity	ICM iopamidol forms iodo-DBPs in chlorinated, chloraminated drinking water that are cytotoxic, genotoxic to mammalian cells	No chronic toxicity of the degradation product on zebrafish even at 100 ppm	Notmicrocidal to bacteria	(Duirk et al., 2011; Steger-Hartmann et al., 1999; Steger-Hartmann et al., 2002)
Artificial sweeteners	Sucralose	Not mutagenic, carcinogenic; no developmental or reproductive toxicity	No adverse effects on reproduction system of rats; not acutely toxic to mice	Low bioaccumulation in mussels, species of *Daphnia*, fish, algae; may be toxic to aquatic species at ≥1123 ppm; may affect locomotion in crustaceans	Not toxic to plant growth; food intake increases in one species of marine copepod	(Shwide-Slavin et al., 2012; Soh et al., 2011; Tollefsen et al., 2012; Wiklund et al., 2012)
Musks & fragrances	Galaxolide	Weak estrogenic effect at concentrations much higher than environmentally relevant levels	Risk ratios for predators on aquatic and soil organisms ≤ 0.01	In marine mussel gills, inhibits activity of multidrug efflux transporters (that protect cells from damage by pumping out pollutants)	-	(Balk & Ford, 1999; Luckenbach & Epel, 2005; Schreurs et al., 2002; Seinen et al., 1999; Witorsch & Thomas, 2010)
UV-filters	4-MBC	Effect on reproductive and thyroid hormone possible after dermal application of mixture of 3 UV-filters	Changes gonadal weight and steroid hormone production in male rats	Potency for estrogenic activity using fish MCF-7 cell lines; antiestrogenic activity using fish hERα; mixture with other UV-filters may risk aquatic environment	Reproduction increased, mortality decreased in worm *Lumbriculus variegates*	(Brausch & Rand, 2011; Fent et al., 2010b; Krause et al., 2012)
Antimicrobial preservatives	Benzylparaben	-	Potential EDC; but concentrations in surface water is much lower than PNEC	EDC in some fishes; toxic to some fish	Toxic to invertebrates	(Brausch & Rand, 2011)
Other personal care products	DEET	Not carcinogenic, developmentally toxic, or mutagenic; seizures at high dose	Not toxic to small mammals	Chronic and acute toxic effects on *Daphnia* and algae at concentrations much higher than aquatic concentrations	Slightly toxic to birds	(Aronson et al., 2012; Costanzo et al., 2007; USEPA, 1998)
FWAs	DSBP	May cause inhibition to estrogenic response	-	May cause inhibition to estrogenic response in rainbow trout	-	(Simmons et al., 2008)
Algal toxins	Microcystin	Liver cancer, death from liver failure, skin damage, respiratory problem	Disrupts hepatocyte cytoskeleton, damages DNA, promotes tumor in rats	Anemia, kidney dysfunction in carps; accumulation in livers of turtles	Accumulation in spleens and livers of ducks, waterbirds	(Chen et al., 2009c; Sedan et al., 2013)
Off flavors	Geosmin	Not toxic to humans	Study on monkey, dog shows non-toxicity	No acute toxicity to fish (copper fin); not mutagenic	Toxic to *Salmonella typhimurium*	(Mochida, 2009)

equivalent level (DWEL) values and/or the acceptable daily intake (ADI) values of the EOCs have also been tabulated in order to better understand their potential health effects. The ADI is defined as the amount of a chemical a human being, including sensitive subgroups and subpopulations such as old people and expectant mothers, can be exposed to on a daily basis over an extended period of time without suffering harmful effects. The DWEL for non-carcinogens is calculated by multiplying the ADI by an assumed body weight of 70 kilograms and dividing by an average daily drinking water intake rate of 2 L per day (Snyder et al., 2008). Among the sixteen compounds listed in Table 3, the occurring concentrations in the surface waters of three compounds, namely bisphenol-A, 4-nonylphenol monoethoxylate (NP1EO) and estrone exceed their respective PNEC values and this may pose a threat to the ecosystem given the fact that all these compounds have the potency to affect the hormonal systems in humans and animals. Also the concentration range of the sunscreen 4-MBC (959–1,287 ng/l) found in the WWTP effluent of North-China exceeds the PNEC value of 4-MBC, which is 560 ng/l (Table 3). Table 3 also depicts the water quality guideline values for all the sixteen compounds which are seen to be higher than the respective surface water occurrence concentrations of the compounds. However, for fipronil and PFOS their respective concentrations in surface waters are close to the DWEL values.

6. Potential health significance of selected EOCs

In this section detection levels of selected EOCs in human fluids (including blood plasma, milk, urine), aquatic life, plants, sediments and suspended solid is summarized (Table 4). The purpose of this section is to demonstrate from existing literature: (1) the EOCs present in the UWC at concentrations which could be of significant health risk, and (2) EOCs that can cause potential public health risks but are currently detected at safe values in typical UWC. A recent comprehensive review on the human risk assessment of endocrine disruptive plastic additives (such as BPA) concludes that even though infants and babies are highly susceptible to BPA exposure via consumption of formula or breast milk, canned and baby food, the calculated hazard index (HI) of the exposure levels is much less than one (0.002–0.26) (Bang et al., 2012). Similarly, adults who are exposed to BPA via the consumption of canned beverages and wine are also safe from harm as the HI is typically within the safe range of 0.002–0.03 (Bang et al., 2012). However, as illustrated in Table 2a, the fact remains that BPA may still pose a carcinogenic risk to humans. In addition, studies on mice show that BPA is capable of binding to DNA via metabolic activation, has estrogenic activity at low concentrations and has the potential to pose an increase in anomalies such as synaptic abnormality (i.e. irregularity in synapses or regions where nerve impulses are transmitted (Sharma et al., 2009)) and meiotic aneuploidy (i.e. abnormality in the number of chromosomes during meiosis or reproduction related cell division (Vandenberg et al., 2007; Sharma et al., 2009)). As depicted in Tables 3 and 4, BPA occurs not only in the receiving surface waters and sediments (Vethaak et al., 2005) of the UWC but also in the serum, urine (Vandenberg et al., 2007) and breast milk of humans (Sun et al., 2004), as well as in fish purchased in local fish markets (Basheer et al., 2004). Since the PNEC of BPA has been reported to be between 60–1500 ng/l, and surface waters across different parts of the world have concentrations ranging from 2.0–4,230 ng/l (Table 3), BPA present in the UWC could pose a potential threat to the ecosystem and needs to be controlled at source. In addition, the concentrations of BPA in human serum and urine have been detected to be as high as 2500 and 3200 ng/l respectively (Vandenberg et al., 2007), possibly due to contaminated water from plastic cans and containers leaching BPA. More research is needed to conclusively prove the adverse effects of BPA on humans and wildlife. In the meantime, it would be prudent to take measures to control the release of BPA to urban surface waters. In a recent critical review on the regulatory structure of BPA, it was reported that BPA release was not strictly regulated in either US or EU but very strictly controlled in Canada, which was the first country to ban the use of BPA in baby bottles in 2008–2009, and limit its emission by manufacturers at 1.75 mg/l in 2009 (Flint et al., 2012).

Galaxolide, with a log K_{OW} value of 5.9, is highly lipophilic and has a high tendency of bioaccumulation. As illustrated in Tables 3 and 4, Galaxolide is present in human blood plasma (Hutter et al., 2005) and breast milk (Zhang et al., 2011), fishes (Moon et al., 2011; Subedi et al., 2012), sediment (Alvarez et al., 2012), trees (Calderón-Preciado et al., 2011) and surface waters (Guo et al., 2012; Heberer, 2002; Kameda et al., 2011; Reiner and Kannan, 2011; Wang and Ding, 2009). However, in spite of its ubiquitous presence in the environment, a series of ecotoxicological studies have shown that galaxolide has a low risk ratio («1) for all aquatic and terrestrial species studied (Balk and Ford, 1999) and hence its use and release to the environment may not require regulation.

Fipronil, a widely used insecticide for urban pest control, landscaping and agriculture, has been detected in human serum (Herin et al., 2011), sediment (Li et al., 2013), corn seeds (Sabatino et al., 2013) and in the surface waters (Moore et al., 2007; Xu et al., 2011), as illustrated in Tables 3 and 4. In a study in Vietnam researching on the presence of insecticide residues in drinking water derived from surface waters, fipronil was detected in 9.5% of the drinking water samples at a median frequency of 160 ng/l (Toan et al., 2013). This finding seems to warrant regulation on the use and release, especially because it has been identified by EPA as a potential human carcinogen (Lee et al., 2010). Although the commonly used insect repellent DEET has been detected in human maternal and cord serum in study in New Jersey, USA (Barr et al., 2010), in mussels, sediments (Klosterhaus et al., 2013), and surface water samples (Aronson et al., 2012; Nakada et al., 2007; Yang et al., 2013), it has been recently concluded that DEET concentrations in surface waters are unlikely exerting acute toxicity (Aronson et al., 2012). It has been calculated that DEET concentrations in aquatic environment would adversely affect aquatic species only at concentrations that are 75,000 or 38,000 or 6,000 times above the highest concentrations reported in surface waters, sewage effluent, or groundwater respectively (Costanzo et al., 2007).

Also as illustrated in Tables 3 and 4, 4-MBC, a UV-filter widely used ingredient in cosmetics and sunscreens, is only removed by 18–82% by conventional WWTPs (Liu et al., 2012) and has been reported to occur in surface waters (Fent et al., 2010a; Kameda et al., 2011; Li et al., 2007), fish (Buser et al., 2006), sediments (Kaiser et al., 2012) and biosolids (Liu et al., 2011). UV-filters can be potentially endocrine disruptive in nature as they have shown hormonal and estrogenic activity *in vitro* (Fent et al., 2010b) and estrogenic activity in fishes (Fent et al., 2010a). Perfluorooctanesulfonate (PFOS) is one of the most widely detected PFC in the aquatic environment (Nguyen et al., 2011; So et al., 2007; Takazawa et al., 2009; Zhang et al., 2012), human serum (Sturm and Ahrens, 2010), fish (Taniyasu et al., 2003) and sediment (Nguyen et al., 2012). The toxic effect of PFOS is well documented for animals and aquatic organisms (Giesy et al., 2010; Lindstrom et al., 2011), and PFOS has also shown to be potential carcinogenic effect on rodents (Lau et al., 2007).

For most EOCs, there is insufficient quantitative toxicological data such as the acceptable daily intake (ADI), tolerable daily intake (TDI), reference dose (RfD) available to establish regulatory drinking water limits. The German Environmental Protection Agency (Umweltbundesamt) has proposed a "health-related indicator value (HRIV)" to assess chemicals for which such data is absent (Umweltbundesamt, 2003). HRIV derivation is based on the worst case assumption (referred to as the "cautionary principle") and the assumption that a person drinking 2 L water per day for 70 years would not experience health related concerns. In the absence of relevant toxicity data, a compound is considered genotoxic and the HRIV is 10–100 ng/L (2-chloroethanol). For compounds with known genotoxicity and with metabolic relevance, the HRIV are below 10 ng/L (NDMA). For compounds with immuno- and/or neurotoxicity, subchronic and chronic toxicity, the ranges HRIV are 0.1–0.3 μg/L, 0.3–1.0 μg/L, and 1.0–3.0 μg/L, respectively (Umweltbundesamt, 2003). If

Table 3
A literature review on the occurrence of EOCs in the urban water supplies, based on reported literature (2001-present).

Chemicals (functions)	Concentration range of chemicals in urban surface waters reported in literature between 2005–2013, ng/l, n/(median concentration) ref.						Water quality guideline, μg/l, ref.	PNEC, μg/l, ref.
	China	Japan	Singapore	Taiwan	Switzerland & Germany	USA		
	Pearl river and tributaries, Dianchilake[a], Haihe river system[b], Lake Taihu[b]	Tamagawa river, Tone river[c], urban streams in Tokushima, Osaka[d]	Marina catchment	Kaopingriver[e], surface waters samples[f]	Glattriver[g], Rhine river and/tributaries[h], entire Rhine catchment[i]	Mississippi river (MR): Louisiana[j], Upper MR basin[k], MR delta[l]; Upper Hudson river[m]; Others[n]		
Bisphenol A (making plastics)	2.2–1030, (132) (Wang et al., 2012b); 278.6–1415.3, (553.3) (Yu et al., 2011); 50.6–530.3, (130.3[a]) (Wang et al., 2012a)[a]	27 ± 19[a,c] (Nakada et al., 2004)	29.6–625, (161) (Xu et al., 2011)	<37–4,230, 120 (Chen et al., 2010a)[e]	9–76, 30 (Voutsa et al., 2006)[g]; 2.0–46, (9.4) (Giger et al., 2009)[g]; 42–229, 5 (Fromme et al., 2002)[h]	0–147.2, (N.R.) (Zhang et al., 2007)[j]	1,800 (DWEL), (Snyder et al., 2008)	0.06–1.5 (Santhi et al., 2012)
PFOS (protective coatings, surfactants)	0.0–99, 12 (So et al., 2007); 1.7–15.1, 26 (Zhang et al., 2012)[a]	0.9–20, 5 (Takazawa et al., 2009)[c]	1–156, (25) (Nguyen et al., 2011)	N.D. ~10, (3.5) (Kunacheva et al., 2012)[f]	27–93, (49[a]) (Huset et al., 2008)[g]; 2–26, N.R. (Skutlarek et al., 2006)[h]	<LOQ-245, (3.01) (Nakayama et al., 2010)[k]	5.25 (DWEL), 0.00015 (ADI) (Schriks et al., 2010)	1.1 (Mhadhbi et al., 2012)
Fipronil (termiticide)	N.A.	N.A.	1–72, (N.R.) (Xu et al., 2011)	N.A.	N.A.	<LOD-11, 9 (Moore et al., 2007)[l]	7 (DWEL), 0.0002 (ADI) (Gupta et al., 2009; Snyder et al., 2008)	0.25[1] (Key et al., 2003)
NP1EO (surfactant)	115.3–448.5, (218[a]) (Wang et al., 2012a)[a]	40–160, 6 (Isobe et al., 2001)	N.A.	<LOD-27,200, 120 (Chen & Yeh, 2010)[e]	<7.3–42, (18) (Giger et al., 2009)[g]; 10–3,270, N.R. (Wenzel et al., 2004)[j]	N.A.	455 (DWEL), 13 (TDI) (Ademollo et al., 2008)	0.33 (Bursch et al., 2004)
Sulfamethoxazole (antibiotic)	111–193[*] ,(134) (Xu et al., 2007)	4–23, (19) (Managaki et al., 2007); <LOQ-7.2, (6.7) (Nakada et al., 2007)[c]	N.A.	~0.5–85, N.R. (Lin et al., 2011)[g]	10–110, (30) (ter Laak et al., 2010)[i]	17–990[l] and N.D.[m], (N.R.) (Oppenheimer et al., 2011)[n]	18,000 (DWEL), (Bruce et al., 2010)	20 (Pal et al., 2010)
Acetaminophen (analgesics, anti-inflammatory)	67–339, 12 (Yang et al., 2013)	<LOQ-52, (22) (Nakada et al., 2007)[c]	N.A.	~0.7–100, N.R. (Lin et al., 2011)[g]	N.D. (Ternes, 1998)[h]	24.7–65.2, (N.R.) (Zhang et al., 2007)[j]	29.1 (DWEL), 0.00083 (ADI), (Murray et al., 2010)	9.2 (Pal et al., 2010)
Estrone (estrogen)	N.D.-75, (2.8) (Wang et al., 2012b); <0.1–21.3, (5.6) (Yu et al., 2011)	22.0–44.6[c], (31.4[a])[c] (Nakada et al., 2004)	<1–304, (N.R.) (Xu et al., 2011)	8.7–144, (46.4[a]) (Chen et al., 2010b)[h]	<LOD (LOD = 1) (Pawlowski et al., 2003)[h]	0–4.7, (N.R.) (Zhang et al., 2007)[j]	0.46 (DWEL), (Snyder et al., 2008)	0.018 (Pal et al., 2010)
Iopromide (ICM)	21.4–1439.3, (89.7) (Yu et al., 2011)	N.A.	N.A.	N.A.	20–1,000 (125) (ter Laak et al., 2010)[i]	N.D.[n](Yang et al., 2011)[n]	250,000 (provisional guideline value) (Schriks et al., 2010)	>10,000 (Steger-Hartmann et al., 1999)
Sucralose (sugar substitute)	300–3,400, (1,100) (Heeb et al., 2012)[b]	N.A.	N.A.	N.A.	<LOD-83, 19 (Loos et al., 2009)[k]	120–10,000[l] and N.D.[m], (N.R.) (Oppenheimer et al., 2011)[n]	525,000 (DWEL), 15 (ADI) (Lachenmeier et al., 2013)	930 (Tollefsen et al., 2012)
Galaxolide (fragrance)	3.13–212.04, (36.15[a]) (Guo et al., 2012)[b]	9.4 ± 9.4[a] (Kameda et al., 2007)[d,c]	N.A.	N.R., (3.2[a]) (Wang & Ding, 2009)[i]	20–12,500, N.R. (Heberer, 2002)[h]	3.95–25.8, 5 (Reiner & Kannan, 2011)[m]	1,800 (DWEL), (Lampard et al., 2010)	6.8 (Balk & Ford, 1999)
4-MBC (sunscreen)	959–1287, (1109[a]) (Li et al., 2007)[**]	N.D., n = 43 (Kameda et al., 2007)[d,c]	N.A.	N.A.	12–17, 10 (Fent et al., 2010a)[g]	N.A.	N.A.	0.56 (Fent et al., 2010b)
Benzylparaben (antimicrobial preservatives)	1.5–5.7, 4 (Yu et al., 2012)[***]	<0.2–2.1, 19 (Yamamoto et al., 2011)[d]	N.A.	N.A.	<0.2–4.4, (0.0) (Giger et al., 2009)[g]	N.A.	N.A.	0.04 (Terasaki et al., 2013)
DEET (mosquito repellant)	0.4–107, 12 (Yang et al., 2013)	<LOQ-36, (18) (Nakada et al., 2007)[c]	N.A.	N.A.	14–30, N.R. (Aronson et al., 2012)[h]	5–200, (N.R.) (Aronson et al., 2012)[o]	3,500 (DWEL), 0.1 (ADI) (Blanset et al., 2007)	500–24,000[2] (Weeks et al., 2012)
DSBP (FWA)	N.A.	6.8–314.1, 19 (Managaki et al., 2006)[e]	N.A.	200–3,700, N.R. (Shu & Ding, 2005)[f]	~450–1200, 68 (Poiger et al., 1999)[g]	N.A.	N.A.	100 (Poiger et al., 1999)

Table 4
EOCs of public health significance.

Compounds	Some examples of detected levels (concentration, type of tissue in case of human/marine life, place of study and reference)		
	Humans	Aquatic species	Sediments and suspended solids, plants
Bisphenol-A	Serum: 0–2,500[a]ng/l, Urine:110–3,200[a]ng/l, review based in different countries (Vandenberg et al., 2007); breast milk: 280–970[a]ng/l (n = 23), Japan (Sun et al., 2004)	Detected in prawn, crab, blood cockle, white clam, squid, fish: 13.3 – 213.1[a] μg/kg ww, purchased from Singapore local supermarkets (Basheer et al., 2004)	Sediment: <1.1–43[a] μg/kg dw, suspended solids: 5.6–56[a] μg/kg dw, Netherlands from multiple marine, estuarine, and fresh surface waters (Vethaak et al., 2005)
Galaxolide	Blood plasma: 420[b]ng/l (Hutter et al., 2005); breast milk: 16–108[a]ng/g lw (n = 5) (Zhang et al., 2011)	Fish tissue: 447[c]ng/g ww, Germany (Subedi et al., 2012); liver tissue of Chinese sturgeon: 33[d]ng/g lw (n = 7), China; blubber of finless porpoises: 37[d]ng/g lw (n = 52), Korea; blubber of California sea lion: 12[d]ng/g lw (n = 5), USA (Moon et al., 2011)	Sediment (at 10–20 cm): 27[e]ng/l, sediment (at 0–10 cm): 21[e]ng/l, USA, (Alvarez et al., 2012); Apple trees irrigated with river water: <0.015 μg/kg, Spain (Calderón-Preciado et al., 2011)
Fipronil	Serum: 0.47[d] μg/l in 33 out of 159 workers of a factory manufacturing fipronil-containing veterinary drugs, France(Herin et al., 2011)	-	Sediment:<reporting limit-9.1 ng/g dw, urban stream of Guangzhou, China (Li et al., 2013); 0.13[d] mg/kg organic carbon, USA (Hintzen et al., 2009); treated corn seeds: 0.002–18[a] mg/kg, Italy (Sabatino et al., 2013)
DEET	Urine: <LOD, for 2535 subjects among general population, USA (Yusa et al., 2012);maternal serum: 1.82–18.84[a], 2.78[b] ng/g (n = 138) and cord serum: 2.06–13.07[a], 2.9[b]ng/g (n = 148), USA (Barr et al., 2010)	Coral, fish, plankton, and detritus samples collected from coral reefs: detected at concentrations less than the method quantitation limit, USA (Bargar et al., 2013); benthic mussel: 3.7–13.7[a], 3.8[b] ng/g ww (100% detection), urban estuary, USA (Klosterhaus et al., 2013)	Sediment: <RL-3.4[a], <RL[b]ng/g dw (40% detection), urban estuary, USA(Klosterhaus et al., 2013)
4-MBC	Breast milk: 6.70–48.37[a]ng/g lw, 20.37% detection, Switzerland (Schlumpf et al., 2010); urine: 4[f]ng/ml, and, plasma (female): 16[f]ng/ml, Denmark (Janjua et al., 2008)	Fish (brown trout): 50–1,800[a]ng/g lw from small rivers with inputs from WWTPs, and, lake fish (white fish and roach): <20–170[a]ng/g lw, Switzerland (Buser et al., 2006)	Lake sediment: 2.0[c]μg/kg dw, river sediment: 1.6[c]μg/kg dw, Germany (Kaiser et al., 2012); biosolid sample: 250[c]ng/g, Australia (Liu et al., 2011)
PFOS	Serum: <4.3–1,656[a], 34.9[d] μg/l, USA, n = 645 (Olsen et al., 2003); breast milk: 330[b]ng/l (n = 13), Hungary(Sturm & Ahrens, 2010)	Whole blood: 30–146[a] μg/l (common sea bass), 455–834 μg/l (blue gill), Japan (Taniyasu et al., 2003)	Sediment top layer (1–10 cm): 858–3,570 ng/kg dw, Singapore (Nguyen et al., 2012)
PFOA	Serum (breastfeeding women): 3.5[b]ng/ml (n = 34), USA; breast milk: 0.047–0.21[a]ng/ml (n = 19), China; cord blood: 0.3–7.1[a]ng/ml (n = 293), USA (von Ehrenstein et al., 2009)	Whole tissue: 90[d]ng/g ww(bottom-dwelling crustacean Diporeia), Canada, <0.2[d]ng/g ww (benthic algae), USA,0.3[d]ng/g ww (zooplankton), USA; fish liver: 6–91[a]ng/g ww, Canada(Houde et al., 2006)	Sediment top layer (1–10 cm): 39–322 ng/kg dw, Singapore (Nguyen et al., 2012)

[a] Concentration range.
[b] Median concentration.
[c] Maximum concentration.
[d] Mean concentration.
[e] Estimated time-weighted average water concentrations measured by polar organic chemical integrative samplers buried in the lake sediment. ww = wet weight; lw = lipid weight; dw = dry weight; n = sample numbers analyzed; LOD: Limit of detection; RL: reporting limit.
[f] Maximum median concentration, for persons exposed to daily whole-body topical application of 2 mg/cm^2 of sunscreen formulation at 10% (w/w) of each of 3 UV-filters for 4 days.

more toxicological data becomes available, HRIVs are modified upwards or remain the same (Dieter, 2013).

7. Conclusions

Using water in closed loops requires efficient wastewater and drinking water treatment, source control, and a detailed understanding of contaminant occurrence, significance, and behavior in the UWC. Assessing occurrence has become possible by the extremely sensitive analytical methods available today, which allow for the detection of thousands of contaminants at trace levels. Assessing the behavior of contaminants in the UWC is lagging and definitive science-based approaches to quantify the human and ecological health significance of these contaminants remain to be developed. This knowledge gap

Notes to Table 3:
Note: n-number of samples.
[a] Mean concentration; N.A. – no occurrence data available.
[b] Dummy footnote.
* Low water season; N.D. – Not detected.
** Due to unavailability of occurrence data for 4-MBC in surface waters in China, we have reported the effluent concentration of a wastewater reclamation plant in north China, collected in July 2005.
*** Due to unavailability of occurrence data for benzylparaben in surface waters in China, we have reported the effluent concentration of WWTPs in Hong Kong, based on SPE method.
[c] STP effluent discharged in the Tamagawa river; LOQ – Limit of quantification.
[d] Data collected across 43 sampling sites along four rivers including Tone, Ara, Tama, and Turumi.
[e] Data collected across 19 locations of the Tokyo Bay where 90% water supply is from Edogawa, Arakawa, Sumidagawa and Tamagawa rivers; N.R.-not reported.
[f] Data collected from river in Taipei; LOD-Limit of detection.
[g] Rivers, reservoirs and dams in Taiwan.
[h] Downstream of Wulo Creek in South Taiwan, with a high discharge of concentrated animal feedlot in its upstream.
[i] Water sample collected from a ditch located 100 m downstream from an effluent outlet of a detergent manufacturer, Taiwan.
[j] River influenced by STP in Germany.
[k] 19 rivers in Germany including Rhine; Various urbanized water sources in USA.
[l] With wastewater discharges.
[m] Without wastewater discharges.
[n] Effluent of wastewater reclamation plant in Gwinnett County, GA, U.S.A.
[o] Main stem of Mississippi river; DWEL: Drinking Water Equivalent Level; ADI: Acceptable Daily Intake; TDI: Tolerable Daily Intake; PNEC: Predicted min. No Effect Concentration.
[1] Since PNEC value for fipronil in aquatic environment is unavailable, this value refers to no observed effect concentration (NOEC) for larvae grass shrimp (*Palaemonetespugio*) as the test object (Key et al., 2003).
[2] This is the chronic NOEC for daphnids and green algae.

creates considerable uncertainties in developing rational management practices of urban waters.

1. Water in the UWC is vulnerable to EOC contamination due to its relatively small volume and limited natural attenuation potential. Protecting urban water supplies from EOC contamination requires tighter controls on sources and product use. For point sources, individual sources may have to be identified by monitoring of sewer systems to banning the discharge of chemicals into the sewer system. EOCs, such as perfluorinated compounds and other surfactants, plasticizers, and pesticides that enter the UWC from non-point sources are difficult to control. Some of these chemicals (perfluorooctanoic acid, perfluoroctanesulfonic acid) persist in the UWC and are difficult to remove by conventional treatment technologies.
2. In some cases, the use of chemicals with high water pollution potential and ecotoxicological risk may have to be restricted. An example may be the wide spread use of antibiotics in animal husbandry (Kemper, 2008).
3. In the UWC, natural attenuation processes are limited by relatively short water transport paths in rivers and residence times. Natural attenuation has been studied only for a limited number of contaminants. For many of the newly discovered EOCs, natural attenuation in the UWC is still poorly understood. This places greater significance on the efficacies of wastewater and drinking water treatment processes.
4. For most EOCs, risk data is inadequate for setting standards and prioritizing treatment needs and for communicating risks to the public. Approaches to set limits for EOCs have been proposed but are still untested and are likely going to be revised. These uncertainties complicate communication with the public and hinder acceptance of drinking water that originates to a significant part from wastewater.

8. Research needs

In order to guide the development of rational water management practices that are protective of human and ecological health, a significant research effort is needed focusing on the following key issues.

1. Extensive and complete occurrence data on different EOCs in drinking water required to identify those that reach the drinking water at potentially significant concentrations. EOC behavior in different UWCs should be studied using consistent approaches.
2. Human health effects of continuing low level exposure to EOCs should be studied with emphasis on those that could enter the food chain indirectly through the consumption of water.
3. Long-term ecotoxicological effects of EOCs and EOC mixtures to wildlife and ecosystem structure and dynamics need to be researched.
4. EOC behavior needs to be monitored in the UWC. This should include compounds which have only been recently discovered, such as, steroidal drugs, anti-psychotic drugs and banned medications, and compounds with a potential of being a contaminant to the UWC in the future such as illicit drugs, melamine or melamine resins or chemicals used in textile dyes.
5. Sources and entry points of EOCs into the UWC requires to be identified. Such studies should quantify mass flow, identify sinks, and removal mechanisms and transformation products.
6. For products that are difficult to control, ecologically friendly alternatives should be found. For example, UV-filters and synthetic musks in cosmetics, shampoos, bath products could be replaced with plant and ayurvedic products such as with neem oil as in pre-modern days to avoid direct effect on humans and prevent their release in the UWC. Similarly, research on green pesticides and natural musks should be carried out.
7. The UWC should be re-engineered to minimize input and maximize natural attenuation. This could include the incorporation of natural attenuation processes into the UWC, such as specially designed wetlands and reservoirs for the removal of EOCs.
8. Wastewater and drinking water treatment technologies need to be evaluated with respect to their removal of EOCs and technologies need to be developed that are capable of removing a broad spectrum of EOCs while minimizing the formation of treatment by-products.
9. Water quality models should include fate and transport models to evaluate relevant EOCs and their impacts on ecosystems and the environment. Development of such models requires an understanding of kinetics and transformation processes which is still lacking for many EOCs.

Acknowledgement

This research is funded by the Singapore National Research Foundation (NRF) and the publication is supported under the Campus for Research Excellence and Technological Enterprise (CREATE) programme, administered by the NUS Environmental Research Institute (NERI). Additional support was obtained from the Alexander von Humboldt Foundation.

References

Ademollo N, et al. Nonylphenol and octylphenol in human breast milk. Environ Int 2008;34(7):984–7.
Al-Rifai JH, Gabelish CL, Schäfer AI. Occurrence of pharmaceutically active and non-steroidal estrogenic compounds in three different wastewater recycling schemes in Australia. Chemosphere 2007;69(5):803–15.
Alvarez DA, et al. Bottom sediment as a source of organic contaminants in Lake Mead, Nevada, USA. Chemosphere 2012;88(5):605–11.
Apelberg BJ, et al. Cord serum concentrations of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in relation to weight and size at birth. Environ Health Perspect 2007;115(11):1670–6.
Aronson D, et al. Environmental release, environmental concentrations, and ecological risk of N, N-diethyl-m-toluamide (DEET). Integr Environ Assess Manag 2012;8(1):135–66.
Aydin E, Talinli I. Analysis, occurrence and fate of commonly used pharmaceuticals and hormones in the Buyukcekmece Watershed, Turkey. Chemosphere 2013;90(6):2004–12.
Balk F, Ford RA. Environmental risk assessment for the polycyclic musks, AHTN and HHCB. II. Effect assessment and risk characterisation. Toxicol Lett 1999;111(1–2):81–94.
Bang DY, et al. Human risk assessment of endocrine-disrupting chemicals derived from plastic food containers. Compr Rev Food Sci Food Saf 2012;11(5):453–70.
Bargar TA, et al. Contaminants assessment in the coral reefs of Virgin Islands National Park and Virgin Islands Coral Reef National Monument. Mar Pollut Bull 2013;70:281–8.
Barr DB, et al. Pesticide concentrations in maternal and umbilical cord sera and their relation to birth outcomes in a population of pregnant women and newborns in New Jersey. Sci Total Environ 2010;408(4):790–5.
Basheer C, Lee HK, Tan KS. Endocrine disrupting alkylphenols and bisphenol-A in coastal waters and supermarket seafood from Singapore. Mar Pollut Bull 2004;48(11–12):1161–7.
Beggel S, et al. Impacts of the phenylpyrazole insecticide fipronil on larval fish: Time-series gene transcription responses in fathead minnow (Pimephales promelas) following short-term exposure. Sci Total Environ 2012;426:160–5.
Blanset DL, Zhang J, Robson MG. Probabilistic estimates of lifetime daily doses from consumption of drinking water containing trace levels of N, N-diethyl-meta-toluamide (DEET), triclosan, or acetaminophen and the associated risk to human health. Hum Ecol Risk Assess 2007;13(3):615–31.
Bound JP, Kitsou K, Voulvoulis N. Household disposal of pharmaceuticals and perception of risk to the environment. Environ Toxicol Pharmacol 2006;21(3):301–7.
Brausch JM, Rand GM. A review of personal care products in the aquatic environment: Environmental concentrations and toxicity. Chemosphere 2011;82(11):1518–32.
Brown KD, et al. Occurrence of antibiotics in hospital, residential, and dairy effluent, municipal wastewater, and the Rio Grande in New Mexico. Sci Total Environ 2006;366(2–3):772–83.
Bruce GM, Pleus RC, Snyder SA. Toxicological relevance of pharmaceuticals in drinking water. Environ Sci Technol 2010;44(14):5619–26.
Buerge IJ, et al. Combined sewer overflows to surface waters detected by the anthropogenic marker caffeine. Environ Sci Technol 2006;40(13):4096–102.
Bursch W, et al. Endocrine disrupters in the aquatic environemtn: The Austrian approach – ARCEM; 2004. p. 293–300.
Buser HR, et al. Occurrence of UV filters 4-methylbenzylidene camphor and octocrylene in fish from various Swiss rivers with inputs from wastewater treatment plants. Environ Sci Technol 2006;40(5):1427–31.
Calderón-Preciado D, et al. Screening of 47 organic microcontaminants in agricultural irrigation waters and their soil loading. Water Res 2011;45(1):221–31.

Chen TC, Yeh YL. Ecological risk, mass loading, and occurrence of nonylphenol (NP), NP mono-, and diethoxylate in kaoping river and its tributaries, taiwan. Water Air Soil Pollut 2010;208(1–4):209–20.
Chen C, et al. A review of spatial and temporal assessment of PFOS and PFOA contamination in China. Chem Ecol 2009a;25(3):163–77.
Chen TC, et al. Variation, correlation, and toxicity of phenolic endocrine-disrupting compounds in surface water. J Environ Sci Health A Tox Hazard Subst Environ Eng 2009b; 44(12):1244–50.
Chen J, et al. Simultaneous determination of microcystin contaminations in various vertebrates (fish, turtle, duck and water bird) from a large eutrophic Chinese lake, Lake Taihu, with toxic Microcystis blooms. Sci Total Environ 2009c;407(10): 3317–22.
Chen TC, et al. Bisphenol A occurred in Kao-Pin River and its tributaries in Taiwan. Environ Monit Assess 2010a;161(1–4):135–45.
Chen TS, et al. High estrogen concentrations in receiving river discharge from a concentrated livestock feedlot. Sci Total Environ 2010b;408(16):3223–30.
Christensen FM. Pharmaceuticals in the environment – A human risk? Regul Toxicol Pharmacol 1998;28(3):212–21.
Clarke BO, Smith SR. Review of 'emerging' organic contaminants in biosolids and assessment of international research priorities for the agricultural use of biosolids. Environ Int 2011;37(1):226–47.
Comeau F, et al. The occurrence of acidic drugs and caffeine in sewage effluents and receiving waters from three coastal watersheds in Atlantic Canada. Sci Total Environ 2008;396(2–3):132–46.
Costanzo SD, et al. Is there a risk associated with the insect repellent DEET (N, N-diethyl-m-toluamide) commonly found in aquatic environments? Sci Total Environ 2007; 384(1–3):214–20.
Daneshvar A, et al. Evaluating pharmaceuticals and caffeine as indicators of fecal contamination in drinking water sources of the Greater Montreal region. Chemosphere 2012; 88(1):131–9.
Davidson K, et al. Harmful algal blooms: How strong is the evidence that nutrient ratios and forms influence their occurrence? Estuar Coast Shelf Sci 2012;115:399–413.
Delgado LF, et al. The removal of endocrine disrupting compounds, pharmaceutically activated compounds and cyanobacterial toxins during drinking water preparation using activated carbon-A review. Sci Total Environ 2012a;435–436:509–25.
Delgado LF, et al. QSAR-like models: A potential tool for the selection of PhACs and EDCs for monitoring purposes in drinking water treatment systems – A review. Water Res 2012b;46(19):6196–209.
Dieter HH. Health related guide values for drinking-water since 1993 as guidance to assess presence of new analytes in drinking-water. Int J Hyg Environ Health 2014; 217(2–3):117–32.
Ding WH, et al. Occurrence and behavior of wastewater indicators in the Santa Ana River and the underlying aquifers. Chemosphere 1999;39(11):1781–94.
Dirtu AC, et al. Analytical methods for selected emerging contaminants in human matrices-A review. Anal Bioanal Chem 2012;404(9):2555–81.
Dobbins LL, et al. Probabilistic ecological hazard assessment of parabens using *Daphnia magna* and Pimephales promelas. Environ Toxicol Chem 2009;28(12):2744–53.
Domene X, et al. Soil pollution by nonylphenol and nonylphenol ethoxylates and their effects to plants and invertebrates. J Soils Sediments 2009;9(6):555–67.
Dow. Product safety assessment, Bisphenol A. Available from http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_08b1/0901b803808b19e8.pdf?filepath=productsafety/pdfs/noreg/233-00250.pdf&fromPage=GetDoc, 2012.
Drewes JE, Fox P, Jekel M. Occurrence of iodinated X-ray contrast media in domestic effluents and their fate during indirect potable reuse. J Environ Sci Health A Tox Hazard Subst Environ Eng 2001;36(9):1633–45.
Drewes JE, Reinhard M, Fox P. Comparing microfiltration-reverse osmosis and soil-aquifer treatment for indirect potable reuse of water. Water Res 2003;37(15):3612–21.
Duirk SE, et al. Formation of toxic iodinated disinfection by-products from compounds used in medical imaging. Environ Sci Technol 2011;45(16):6845–54.
Dussault ÈB, et al. In vivo estrogenicity of nonylphenol and its ethoxylates in the Canadian environment. Hum Ecol Risk Assess 2005;11(2):353–64.
Ela WP, et al. Toward identifying the next generation of superfund and hazardous waste site contaminants. Environ Health Perspect 2011;119(1):6–10.
Farré M, et al. Achievements and future trends in the analysis of emerging organic contaminants in environmental samples by mass spectrometry and bioanalytical techniques. J Chromatogr A 2012;1259:86–99.
Fent K, Zenker A, Rapp M. Widespread occurrence of estrogenic UV-filters in aquatic ecosystems in Switzerland. Environ Pollut 2010a;158(5):1817–24.
Fent K, et al. A tentative environmental risk assessment of the UV-filters 3-(4-methylbenzylidene-camphor), 2-ethyl-hexyl-4-trimethoxycinnamate, benzophenone-3, benzophenone-4 and 3-benzylidene camphor. Mar Environ Res 2010b;69(Suppl. 1): S4–6.
Fernandes D, et al. Metabolism of the polycyclic musk galaxolide and its interference with endogenous and xenobiotic metabolizing enzymes in the European sea bass (Dicentrarchus labrax). Environ Pollut 2013;174:214–21.
Flint S, et al. Bisphenol A exposure, effects, and policy: A wildlife perspective. J Environ Manag 2012;104:19–34.
Fromme H, et al. Occurrence of phthalates and bisphenol A and F in the environment. Water Res 2002;36(6):1429–38.
Gago-Ferrero P, Díaz-Cruz MS, Barceló D. An overview of UV-absorbing compounds (organic UV filters) in aquatic biota. Anal Bioanal Chem 2012;404(9):2597–610.
Galus M, et al. Chronic, low concentration exposure to pharmaceuticals impacts multiple organ systems in zebrafish. Aquat Toxicol 2013;132–133:200–11.
Giesy JP, et al. Aquatic toxicology of perfluorinated chemicals; 2010. p. 1–52.
Giger W, et al. Environmental fate of phenolic endocrine disruptors: Field and laboratory studies. Philos Trans R Soc A Math Phys Eng Sci 2009;367(1904):3941–63.
Gross B, et al. Occurrence and fate of pharmaceuticals and alkylphenol ethoxylate metabolites in an effluent-dominated river and wetland. Environ Toxicol Chem 2004;23(9): 2074–83.
Grünheid S, Amy G, Jekel M. Removal of bulk dissolved organic carbon (DOC) and trace organic compounds by bank filtration and artificial recharge. Water Res 2005; 39(14):3219–28.
Guo GH, et al. Screening level ecological risk assessment for synthetic musks in surface water of Lake Taihu, China. Stoch Environ Res Risk Assess 2012:1–9.
Gupta S, et al. Persistence of new insecticides and their efficacy against insect pests of okra. Bull Environ Contam Toxicol 2009;82(2):243–7.
Hamid H, Eskicioglu C. Fate of estrogenic hormones in wastewater and sludge treatment: A review of properties and analytical detection techniques in sludge matrix. Water Res 2012;46(18):5813–33.
Hanselman TA, Graetz DA, Wilkie AC. Manure-borne estrogens as potential environmental contaminants: A review. Environ Sci Technol 2003;37(24):5471–8.
Hass U, Duennbier U, Massmann G. Occurrence and distribution of psychoactive compounds and their metabolites in the urban water cycle of Berlin (Germany). Water Res 2012;46(18):6013–22.
Hayakawa K, et al. Distribution and fluxes of fluorescent whitening agents discharged from domestic wastewater into small rivers with seasonal changes of flow rates. Limnology 2007;8(3):251–9.
Heberer T. Occurrence, fate, and assessment of polycyclic musk residues in the aquatic environment of urban areas – a review. Acta Hydrochim Hydrobiol 2002;30(5–6): 227–43.
Heberer T, Reddersen K, Mechlinski A. From municipal sewage to drinking water: Fate and removal of pharmaceutical residues in the aquatic environment in urban areas; 2002. p. 81–8.
Heeb F, et al. Organic micropollutants in rivers downstream of the megacity Beijing: Sources and mass fluxes in a large-scale wastewater irrigation system. Environ Sci Technol 2012;46(16):8680–8.
Herin F, et al. Thyroid function tests in persons with occupational exposure to fipronil. Thyroid 2011;21(7):701–6.
Hernando MD, et al. Environmental risk assessment of emerging pollutants in water: Approaches under horizontal and vertical EU legislation. Crit Rev Environ Sci Technol 2011;41(7):699–731.
Hintzen EP, Lydy MJ, Belden JB. Occurrence and potential toxicity of pyrethroids and other insecticides in bed sediments of urban streams in central Texas. Environ Pollut 2009; 157(1):110–6.
Houde M, et al. Biological monitoring of polyfluoroalkyl substances: A review. Environ Sci Technol 2006;40(11):3463–73.
Houtman CJ. Emerging contaminants in surface waters and their relevance for the production of drinking water in Europe. J Integr Environ Sci 2010;7(4):271–95.
Huschek G, et al. Environmental risk assessment of medicinal products for human use according to European Commission recommendations. Environ Toxicol 2004;19(3): 226–40.
Huset CA, et al. Occurrence and mass flows of fluorochemicals in the Glatt Valley Watershed, Switzerland. Environ Sci Technol 2008;42(17):6369–77.
Hutter HP, et al. Blood concentrations of polycyclic musks in healthy young adults. Chemosphere 2005;59(4):487–92.
Isobe T, Nishiyama H, Nakashima A, Takada H. Distribution and behavior of nonylphenol, octylphenol, and nonylphenol monoethoxylate in Tokyo metropolitan area: Their association with aquatic particles and sedimentary distributions. Environ Sci Technol 2001;35(6):1041–9.
Jacob CRO, Soares HM, Carvalho SM, Nocelli RCF, Malaspina O. Acute toxicity of fipronil to the stingless bee *Scaptotrigona postica latreille*. Bull Environ Contam Toxicol 2013; 90(1):69–72.
Janjua NR, Kongshoj B, Andersson AM, Wulf HC. Sunscreens in human plasma and urine after repeated whole-body topical application. J Eur Acad Dermatol Venereol 2008; 22(4):456–61.
Jekel M, Ruhl AS, Meinel F, Zietzschmann F, Lima SP, Baur N, et al. Anthropogenic organic micro-pollutants and pathogens in the urban water cycle: Assessment, barriers and risk communication (ASKURIS). Environ Sci Eur 2013;25(1).
Jurado A, Vàzquez-Suñé E, Carrera J, López de Alda M, Pujades E, Barceló D. Emerging organic contaminants in groundwater in Spain: A review of sources, recent occurrence and fate in a European context. Sci Total Environ 2012;440:82–94.
Jüttner F, Watson SB. Biochemical and ecological control of geosmin and 2-methylisoborneol in source waters. Appl Environ Microbiol 2007;73(14): 4395–406.
Kaiser D, Wappelhorst O, Oetken M, Oehlmann J. Occurrence of widely used organic UV filters in lake and river sediments. Environ Chem 2012;9(2):139–47.
Kameda Y, Tamada M, Kanai Y, Masunaga S. Organic UV filters in surface waters, sediments, and core sediments in Tokyo Bay, —organic UV filters are New POPs? Organohalogen Compd 2007;69:263–6.
Kameda Y, Kimura K, Miyazaki M. Occurrence and profiles of organic sun-blocking agents in surface waters and sediments in Japanese rivers and lakes. Environ Pollut 2011; 159(6):1570–6.
Kemper N. Veterinary antibiotics in the aquatic and terrestrial environment. Ecol Indic 2008;8(1):1–13.
Key PB, Chung KW, Opatkiewicz, AD, Wirth EF, Fulton MH. Toxicity of the insecticides fipronil and endosulfan to selected life stages of the grass shrimp (Palaemonetes pugio). Bull Environ Contam Toxicol 2003;70(3):533–40.
Kim S, Aga DS. Potential ecological and human health impacts of antibiotics and antibiotic-resistant bacteria from wastewater treatment plants. J Toxicol Environ Health B Crit Rev 2007;10(8):559–73.
Kim P, Park Y, Ji K, Seo J, Lee S, Choi K, et al. Effect of chronic exposure to acetaminophen and lincomycin on Japanese medaka (Oryzias latipes) and freshwater cladocerans

Daphnia magna and Moina macrocopa, and potential mechanisms of endocrine disruption. Chemosphere 2012;89(1):10–8.

Kloepfer A, Gnirss R, Jekel M, Reemtsma T. Occurrence of benzothiazoles in municipal wastewater and their fate in biological treatment; 2004. p. 203–8.

Kloepfer A, Jekel M, Reemtsma T. Occurrence, sources, and fate of benzothiazoles in municipal wastewater treatment plants. Environ Sci Technol 2005;39(10):3792–8.

Klosterhaus SL, Grace R, Hamilton MC, Yee D. Method validation and reconnaissance of pharmaceuticals, personal care products, and alkylphenols in surface waters, sediments, and mussels in an urban estuary. Environ Int 2013;54:92–9.

Kokotou MG, Asimakopoulos AG, Thomaidis NS. Artificial sweeteners as emerging pollutants in the environment: Analytical methodologies and environmental impact. Anal Methods 2012;4(10):3057–70.

Kosjek T, Heath E. Occurrence, fate and determination of cytostatic pharmaceuticals in the environment. TrAC Trends Anal Chem 2011;30(7):1065–87.

Kramer JB, Canonica S, Hoigné J. Degradation of fluorescent whitening agents in sunlit natural waters. Environ Sci Technol 1996;30(7):2227–34.

Krause M, Klit A, Blomberg Jensen M, Søeborg T, Frederiksen H, Schlumpf M, et al. Sunscreens: Are they beneficial for health? An overview of endocrine disrupting properties of UV-filters. Int J Androl 2012;35(3):424–36.

Kümmerer K. The presence of pharmaceuticals in the environment due to human use – present knowledge and future challenges. J Environ Manag 2009;90(8):2354–66.

Kunacheva C, Fujii S, Tanaka S, Seneviratne STMLD, Lien NPH, Nozoe M, et al. Worldwide surveys of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) in water environment in recent years. Water Sci Technol 2012;66(12):2764–71.

Kunkel U, Radke M. Biodegradation of acidic pharmaceuticals in bed sediments: Insight from a laboratory experiment. Environ Sci Technol 2008;42(19):7273–9.

Lachenmeier DW, Monakhova YB, Markova M, Kuballa T, Rehm J. What happens if people start drinking mouthwash as surrogate alcohol? A quantitative risk assessment. Food Chem Toxicol 2013;51(1):173–8.

Lampard J, Leusch FDL, Roiko A, Chapman HF. Contaminants of concern in recycled water. Water 2010;37(8):54–60.

Lapworth DJ, Baran N, Stuart ME, Ward RS. Emerging organic contaminants in groundwater: A review of sources, fate and occurrence. Environ Pollut 2012;163:287–303.

Lau C, Anitole K, Hodes C, Lai D, Pfahles-Hutchens A, Seed J. Perfluoroalkyl acids: A review of monitoring and toxicological findings. Toxicol Sci 2007;99(2):366–94.

Lee SJ, Mulay P, Diebolt-Brown B, Lackovic MJ, Mehler LN, Beckman J, et al. Acute illnesses associated with exposure to fipronil-surveillance data from 11 states in the United States, 2001–2007. Clin Toxicol 2010;48(7):737–44.

Lepom P, Brown B, Hanke G, Loos R, Quevauviller P, Wollgast J. Needs for reliable analytical methods for monitoring chemical pollutants in surface water under the European Water Framework Directive. J Chromatogr A 2009;1216(3):302–15.

Li W, Ma Y, Guo C, Hu W, Liu K, Wang Y, et al. Occurrence and behavior of four of the most used sunscreen UV filters in a wastewater reclamation plant. Water Res 2007;41(15):3506–12.

Li H, Sun B, Lydy MJ, You J. Sediment-associated pesticides in an urban stream in Guangzhou, china: Implication of a shift in pesticide Use patterns. Environ Toxicol Chem 2013;32(5):1040–7.

Lin AYC, Plumlee MH, Reinhard M. Natural attenuation of pharmaceuticals and alkylphenol polyethoxylate metabolites during river transport: Photochemical and biological transformation. Environ Toxicol Chem 2006;25(6):1458–64.

Lin AYC, Panchangam SC, Ciou PS. High levels of perfluorochemicals in Taiwan's wastewater treatment plants and downstream rivers pose great risk to local aquatic ecosystems. Chemosphere 2010a;80(10):1167–74.

Lin AYC, Wang XH, Lin CF. Impact of wastewaters and hospital effluents on the occurrence of controlled substances in surface waters. Chemosphere 2010b;81(5):562–70.

Lin AYC, Tsai YT, Yu TH, Wang XH, Lin CF. Occurrence and fate of pharmaceuticals and personal care products in Taiwan's aquatic environment. Desalin Water Treat 2011;32(1–3):57–64.

Lindstrom AB, Strynar MJ, Libelo EL. Polyfluorinated compounds: Past, present, and future. Environ Sci Technol 2011;45(19):7954–61.

Linley-Adams G. Nonylphenol Ethoxylates (NPEs), briefing for the World Wildlife Fund (WWF); 1999.

Liu YS, Ying GG, Shareef A, Kookana RS. Simultaneous determination of benzotriazoles and ultraviolet filters in ground water, effluent and biosolid samples using gas chromatography-tandem mass spectrometry. J Chromatogr A 2011;1218(31):5328–35.

Liu YS, Ying GG, Shareef A, Kookana RS. Occurrence and removal of benzotriazoles and ultraviolet filters in a municipal wastewater treatment plant. Environ Pollut 2012;165:225–32.

Loos R, Gawlik BM, Boettcher K, Locoro G, Contini S, Bidoglio G. Sucralose screening in European surface waters using a solid-phase extraction-liquid chromatography-triple quadrupole mass spectrometry method. J Chromatogr A 2009;1216(7):1126–31.

Luckenbach T, Epel D. Nitromusk and polycyclic musk compounds as long-term inhibitors of cellular xenobiotic defense systems mediated by multidrug transporters. Environ Health Perspect 2005;113(1):17–24.

Managaki S, Takada H, Kim DM, Horiguchi T, Shiraishi H. Three-dimensional distributions of sewage markers in Tokyo Bay water – Fluorescent whitening agents (FWAs). Mar Pollut Bull 2006;52(3):281–92.

Managaki S, Murata A, Takada H, Bui CT, Chiem NH. Distribution of macrolides, sulfonamides, and trimethoprim in tropical waters: Ubiquitous occurrence of veterinary antibiotics in the Mekong Delta. Environ Sci Technol 2007;41(23):8004–10.

Mhadhbi L, Rial D, Pérez S, Beiras R. Ecological risk assessment of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) in marine environment using Isochrysis galbana, Paracentrotus lividus, Siriella armata and Psetta maxima. J Environ Monit 2012;14(5):1375–82.

Michael I, Rizzo L, McArdell CS, Manaia CM, Merlin C, Schwartz T, et al. Urban wastewater treatment plants as hotspots for the release of antibiotics in the environment: A review. Water Res 2013;47(3):957–95.

Mochida K. Evaluation of the cytotoxicity of geosmin and 2-methylisoborneol using cultured human, monkey, and dog cells. Biocontrol Sci 2009;14(1):35–8.

Montgomery-Brown J, Reinhard M. Occurrence and behavior of alkylphenol polyethoxylates in the environment. Environ Eng Sci 2003;20(5):471–86.

Moody CA, Field JA. Determination of perfluorocarboxylates in groundwater impacted by fire- fighting activity. Environ Sci Technol 1999;33(16):2800–6.

Moon HB, An YR, Par, KJ, Choi SG, et al. Occurrence and accumulation features of polycyclic aromatic hydrocarbons and synthetic musk compounds in finless porpoises (Neophocaena phocaenoides) from Korean coastal waters. Mar Pollut Bull 2011;62(9):1963–8.

Moore MT, Lizotte Jr RE, Knight SS, Smith Jr S, Cooper CM. Assessment of pesticide contamination in three Mississippi Delta oxbow lakes using Hyalella azteca. Chemosphere 2007;67(11):2184–91.

Moreno-González R, Campillo JA, García V, León VM. Seasonal input of regulated and emerging organic pollutants through surface watercourses to a Mediterranean coastal lagoon. Chemosphere 2013;92(3):247–57.

Murphy EA, Post GB, Buckley BT, Lippincott RL, Robson MG. Future challenges to protecting public health from drinking-water contaminants; 2012. p. 209–24.

Murray KE, Thomas SM, Bodour AA. Prioritizing research for trace pollutants and emerging contaminants in the freshwater environment. Environ Pollut 2010;158(12):3462–71.

Nakada N, Nyunoya H, Nakamura M, Hara A, Iguchi T, Takada H. Identification of estrogenic compounds in wastewater effluent. Environ Toxicol Chem 2004;23(12):2807–15.

Nakada N, Komori K, Suzuki Y, Konishi C, Houwa I, Tanaka H. Occurrence of 70 pharmaceutical and personal care products in Tone River basin in Japan. Water Sci Technol 2007;56:133–40.

Nakada N, Kiri K, Shinohara H, Harada A, Kuroda K, Takizawa S, et al. Evaluation of pharmaceuticals and personal care products as water-soluble molecular markers of sewage. Environ Sci Technol 2008;42(17):6347–53.

Nakayama SF, et al. Determination of Perfluorinated compounds in the upper Mississippi River Basin. Environ Sci Technol 2010;44(11):4103–9.

Nguyen VT, Reinhard M, Karina GYH. Occurrence and source characterization of perfluorochemicals in an urban watershed. Chemosphere 2011;82(9):1277–85.

Nguyen VT, Gin KYH, Reinhard M, Liu C. Occurrence, fate, and fluxes of perfluorochemicals (PFCs) in an urban catchment: Marina Reservoir, Singapore. Water Sci Technol 2012;66(11):2439–46.

OCWD. Groundwater management plan. Fountain Valley, CA, USA: Orange County Water District; 2005.

OCWD. 2011–2012 Engineer's Report on the Groundwater Conditions, Water Supply and Basin Utilization in the Orange County Water District; 2013a [Fountain Valley, CA, USA].

OCWD. Orange County water district budget report fiscal year 2012–13; 2013b [Fountain Valley, CA, USA].

OECD. Results of the 2006 survey on production and use of PFOS, PFAS, PFOA, PFCA, their related substances and products/mixtures containing these substances. OECD environment, health and safety publications series on risk management; 2006.

OECD. PFCs: Outcome of the 2009 survey. Survey on the production, use and release of PFOS, PFAS, PFOA, PFCA, their related substances and products/mixtures containing these substances. OECD environment, health and safety publications series on risk management; 2011.

Olsen GW, Church TR, Miller JP, Burris JM, Hansen KJ, Lundberg JK, et al. Perfluorooctanesulfonate and other fluorochemicals in the serum of American Red Cross adult blood donors. Environ Health Perspect 2003;111(16):1892–901.

Oppenheimer J, Eaton A, Badruzzaman M, Haghani AW, Jacangelo JG. Occurrence and suitability of sucralose as an indicator compound of wastewater loading to surface waters in urbanized regions. Water Res 2011;45(13):4019–27.

Ortiz de García S, Pinto Pinto G, García Encina P, Irusta Mata R. Consumption and occurrence of pharmaceutical and personal care products in the aquatic environment in Spain. Sci Total Environ 2013;444:451–65.

Pal A, Gin KYH, Lin AYC, Reinhard M. Impacts of emerging organic contaminants on freshwater resources: Review of recent occurrences, sources, fate and effects. Sci Total Environ 2010;408(24):6062–9.

Pan S, Sun Y, Zhang G, Li J, Xie Q, Chakraborty P. Assessment of 2-(4-morpholinyl) benzothiazole (24MoBT) and N-cyclohexyl-2-benzothiazolamine (NCBA) as traffic tracers in metropolitan cities of China and India. Atmos Environ 2012;56:246–9.

Parinet J, Rodriguez MJ, Sérodes J. Influence of water quality on the presence of off-flavour compounds (geosmin and 2-methylisoborneol). Water Res 2010;44(20):5847–56.

Park S, Choi K. Hazard assessment of commonly used agricultural antibiotics on aquatic ecosystems. Ecotoxicology 2008;17(6):526–38.

Pawlowski S, Ternes T, Bonerz M, Kluczka T, van der Burg B, Nau H, et al. Combined in situ and in vitro assessment of the estrogenic activity of sewage and surface water samples. Toxicol Sci 2003;75(1):57–65.

Peng X, Yu Y, Tang C, Tan J, Huang Q, Wang Z. Occurrence of steroid estrogens, endocrine-disrupting phenols, and acid pharmaceutical residues in urban riverine water of the Pearl River Delta, South China. Sci Total Environ 2008;397(1–3):158–66.

Pérez S, Barceló D. Fate and occurrence of X-ray contrast media in the environment. Anal Bioanal Chem 2007;387(4):1235–46.

Plumlee MH, López-Mesas M, Heidlberger A, Ishida KP, Reinhard M. N-nitrosodimethylamine (NDMA) removal by reverse osmosis and UV treatment and analysis via LC-MS/MS. Water Res 2008;42(1–2):347–55.

Poiger T, Kari FG, Giger W. Fate of fluorescent whitening agents in the River Glatt. Environ Sci Technol 1999;33(4):533–9.

Pomati F, Castiglioni S, Zuccato E, Fanelli R, Vigetti D, Rossetti C, et al. Effects of a complex mixture of therapeutic drugs at environmental levels on human embryonic cells. Environ Sci Technol 2006;40(7):2442–7.

Post GB, Cohn PD, Cooper KR. Perfluorooctanoic acid (PFOA), an emerging drinking water contaminant: A critical review of recent literature. Environ Res 2012;116:93–117.

PUB. The Singapore water story. Available from http://www.pub.gov.sg/water/Pages/singaporewaterstory.aspx, 2013.

Reemtsma T, et al. Microbial transformations and biological effects of fungicide-derived benzothiazoles determined in industrial wastewater. Environ Sci Technol 1995;29(2):478–85.

Reemtsma T, et al. Polar pollutants in municipal wastewater and the water cycle: Occurrence and removal of benzotriazoles. Water Res 2010;44(2):596–604.

Reiner JL, Kannan K. Polycyclic musks in water, sediment, and fishes from the upper Hudson River, New York, USA. Water Air Soil Pollut 2011;214(1–4):335–42.

Richardson SD. Water analysis: Emerging contaminants and current issues. Anal Chem 2003;75(12):2831–57.

Richardson SD. Environmental mass spectrometry: Emerging contaminants and current issues. Anal Chem 2012;84(2):747–78.

Richter D, Massmann G, Dünnbier U. Identification and significance of sulphonamides (p-TSA, o-TSA, BSA) in an urban water cycle (Berlin, Germany). Water Res 2008;42(6–7):1369–78.

Rodriguez-Moza S, Weinberg HS. Meeting report: Pharmaceuticals in water-an interdisciplinary approach to a public health challenge. Environ Health Perspect 2010;118(7):1016–20.

Sabatini SE, et al. Microcystin accumulation and antioxidant responses in the freshwater clam Diplodon chilensis patagonicus upon subchronic exposure to toxic Microcystis aeruginosa. Ecotoxicol Environ Saf 2011;74(5):1188–94.

Sabatino L, et al. Survey of neonicotinoids and fipronil in corn seeds for agriculture. Food Addit Contam Part B Surveill 2013;6(1):11–6.

Sablayrolles C, et al. Priority organic pollutants in the urban water cycle (Toulouse, France). Water Sci Technol 2011;64(3):541–56.

Santhi VA, et al. Occurrence of bisphenol A in surface water, drinking water and plasma from Malaysia with exposure assessment from consumption of drinking water. Sci Total Environ 2012;427–428:332–8.

Sapkota A, et al. Aquaculture practices and potential human health risks: Current knowledge and future priorities. Environ Int 2008;34(8):1215–26.

Schlumpf M, et al. Exposure patterns of UV filters, fragrances, parabens, phthalates, organochlor pesticides, PBDEs, and PCBs in human milk: Correlation of UV filters with use of cosmetics. Chemosphere 2010;81(10):1171–83.

Schreurs RHMM, et al. Transcriptional activation of estrogen receptor ERα and ERβ by polycyclic musks is cell type dependent. Toxicol Appl Pharmacol 2002;183(1):1–9.

Schriks M, et al. Toxicological relevance of emerging contaminants for drinking water quality. Water Res 2010;44(2):461–76.

Searby L. Emerging markets and sugar prices drive sucralose takeup, JK Sucralose. Available from http://www.foodnavigator-asia.com/Markets/Emerging-markets-and-sugar-prices-drive-sucralose-takeup-JK-Sucralose, 2011.

Sedan D, et al. Biomarkers of prolonged exposure to microcystin-LR in mice. Toxicon 2013;68:9–17.

Seinen W, et al. AHTN and HHCB show weak estrogenic – But no uterotrophic activity. Toxicol Lett 1999;111(1–2):161–8.

Shannon MA, et al. Science and technology for water purification in the coming decades. Nature 2008;452(7185):301–10.

Sharma VK, et al. Nonylphenol, octylphenol, and bisphenol-A in the aquatic environment: A review on occurrence, fate, and treatment. J Environ Sci Health A Tox Hazard Subst Environ Eng 2009;44(5):423–42.

Shu WC, Ding WH. Determination of fluorescent whitening agents in laundry detergents and surface waters by solid-phase extraction and ion-pair high-performance liquid chromatography. J Chromatogr A 2005;1088(1–2):218–23.

Shwide-Slavin C, Swift C, Ross T. Nonnutritive sweeteners: Where are we today? Diabetes Spectr 2012;25(2):104–10.

Simmons DBD, et al. Interaction of stilbene compounds with human and rainbow trout estrogen receptors. Environ Toxicol Chem 2008;27(2):442–51.

Skutlarek D, Exner M, Färber H. Perfluorinated surfactants in surface and drinking waters. Environ Sci Pollut Res 2006;13(5):299–307.

Snyder SA, et al. Toxicological relevance of EDCs and pharmaceuticals in drinking water; 2008.

So MK, et al. Perfluorinated compounds in the Pearl River and Yangtze River of China. Chemosphere 2007;68(11):2085–95.

Soh L, et al. Fate of sucralose through environmental and water treatment processes and impact on plant indicator species. Environ Sci Technol 2011;45(4):1363–9.

Steger-Hartmann T, Länge R, Schweinfurth H. Environmental risk assessment for the widely used iodinated X-ray contrast agent iopromide (ultravist). Ecotoxicol Environ Saf 1999;42(3):274–81.

Steger-Hartmann T, et al. Investigations into the environmental fate and effects of iopromide (ultravist), a widely used iodinated X-ray contrast medium. Water Res 2002;36(1):266–74.

Sturm R, Ahrens L. Trends of polyfluoroalkyl compounds in marine biota and in humans. Environ Chem 2010;7(6):457–84.

Subedi B, et al. Occurrence of pharmaceuticals and personal care products in German fish tissue: A national study. Environ Sci Technol 2012;46(16):9047–54.

Sun Y, et al. Determination of bisphenol A in human breast milk by HPLC with column-switching and fluorescence detection. Biomed Chromatogr 2004;18(8):501–7.

Tadeo JL, et al. Analysis of emerging organic contaminants in environmental solid samples. Cent Eur J Chem 2012;10(3):480–520.

Takazawa Y, et al. Occurrence and distribution of perfluorooctane sulfonate and perfluorooctanoic acid in the rivers of Tokyo. Water Air Soil Pollut 2009;202(1–4):57–67.

Taniyasu S, et al. A survey of perfluorooctane sulfonate and related perfluorinated organic compounds in water, fish, birds, and humans from Japan. Environ Sci Technol 2003;37(12):2634–9.

TenEyck MC, Markee TP. Toxicity of nonylphenol, nonylphenol monoethoxylate, and nonylphenol diethoxylate and mixtures of these compounds to Pimephales promelas (Fathead Minnow) and *Ceriodaphnia dubia*. Arch Environ Contam Toxicol 2007;53(4):599–606.

ter Laak TL, et al. Relating environmental concentrations of pharmaceuticals to consumption: A mass balance approach for the river Rhine. Environ Int 2010;36(5):403–9.

Terasaki M, et al. Chronic toxicity of parabens and their chlorinated by-products in *Ceriodaphnia dubia*. Environ Toxicol 2013. [in press].

Ternes TA. Occurrence of drugs in German sewage treatment plants and rivers. Water Res 1998;32(11):3245–60.

Thomaidis NS, Asimakopoulos AG, Bletsou AA. Emerging contaminants: A tutorial mini-review. Global Nest J 2012;14(1):72–9.

Tingle CCD, et al. Health and environmental effects of fipronil. UK: Pesticide Action Network; 2000.

Tingle CC, et al. Fipronil: environmental fate, ecotoxicology, and human health concerns. Rev Environ Contam Toxicol 2003;176:1–66.

Toan PV, et al. Pesticide management and their residues in sediments and surface and drinking water in the Mekong Delta, Vietnam. Sci Total Environ 2013;452–453:28–39.

Tollefsen KE, Nizzetto L, Huggett DB. Presence, fate and effects of the intense sweetener sucralose in the aquatic environment. Sci Total Environ 2012;438:510–6.

Tortajada C. Water management in Singapore. Int J Water Resour Dev 2006;22(2):227–40.

Umweltbundesamt. Bewertung der Anwesenheit teil- oder nicht bewertbarer Stoffe im Trinkwasser aus gesundheitlicher Sicht. Bundesgesundheitsblatt – Gesundheitsforschung – Gesundheitsschutz. Germany: Umweltbundesamt; 2003. p. 249–51.

USEPA. Reregistration eligibility decision (RED) for DEET; 1998.

USEPA. Bisphenol A action plan; 2010.

Vandenberg LN, et al. Human exposure to bisphenol A (BPA). Reprod Toxicol 2007;24(2):139–77.

Vethaak AD, et al. An integrated assessment of estrogenic contamination and biological effects in the aquatic environment of The Netherlands. Chemosphere 2005;59(4):511–24.

von Ehrenstein OS, et al. Polyfluoroalkyl chemicals in the serum and milk of breastfeeding women. Reprod Toxicol 2009;27(3–4):239–45.

Voutsa D, et al. Benzotriazoles, alkylphenols and bisphenol A in municipal wastewaters and in the Glatt River, Switzerland. Environ Sci Pollut Res 2006;13(5):333–41.

Wang YC, Ding WH. Determination of synthetic polycyclic musks in water by microwave-assisted headspace solid-phase microextraction and gas chromatography–mass spectrometry. J Chromatogr A 2009;1216(40):6858–63.

Wang B, et al. Seasonal distribution, source investigation and vertical profile of phenolic endocrine disrupting compounds in Dianchi Lake, China. J Environ Monit 2012a;14(4):1275–82.

Wang L, et al. Monitoring of selected estrogenic compounds and estrogenic activity in surface water and sediment of the Yellow River in China using combined chemical and biological tools. Environ Pollut 2012b;165:241–9.

Weeks JA, Guiney PD, Nikiforovz AI. Assessment of the environmental fate and ecotoxicity of N, N-diethyl-m-toluamide (DEET). Integr Environ Assess Manag 2012;8(1):120–34.

Weissbrodt D, et al. Mass flows of x-ray contrast media and cytostatics in hospital wastewater. Environ Sci Technol 2009;43(13):4810–7.

Wenzel A, et al. Retrospenctive monitoring of alkylphenols and alkylphenol monothoxylates in aquatic biota from 1985 to 2001: Results from the German environmental specimen bank. Environ Sci Technol 2004;38(6):1654–61.

Wiklund AKE, et al. Sucralose – An ecotoxicological challenger? Chemosphere 2012;86(1):50–5.

Witorsch RJ, Thomas JA. Personal care products and endocrine disruption: A critical review of the literature. Crit Rev Toxicol 2010;40(Suppl. 3):1–30.

Wu J, Zhang L, Yang Z. A review on the analysis of emerging contaminants in aquatic environment. Crit Rev Anal Chem 2010;40(4):234–45.

Wu S, et al. Effects of bisphenol A on the proliferation and cell cycle of HBL-100 cells. Food Chem Toxicol 2012;50(9):3100–5.

Xu Wh, et al. Determination of selected antibiotics in the Victoria Harbour and the Pearl River, South China using high-performance liquid chromatography-electrospray ionization tandem mass spectrometry. Environ Pollut 2007;145(3):672–9.

Xu Y, et al. Occurrence of emerging organic contaminants in a tropical urban catchment in Singapore. Chemosphere 2011;83(7):963–9.

Yamamoto H, et al. Persistence and partitioning of eight selected pharmaceuticals in the aquatic environment: Laboratory photolysis, biodegradation, and sorption experiments. Water Res 2009;43(2):351–62.

Yamamoto H, et al. Aquatic toxicity and ecological risk assessment of seven parabens: Individual and additive approach. Sci Total Environ 2011;410–411:102–11.

Yang X, et al. Occurrence and removal of pharmaceuticals and personal care products (PPCPs) in an advanced wastewater reclamation plant. Water Res 2011;45(16):5218–28.

Yang X, et al. Occurrence and fate of PPCPs and correlations with water quality parameters in urban riverine waters of the Pearl River Delta, South China. Environ Sci Pollut Res 2013;20(8):5864–75.

Yu Y, et al. Occurrence and behavior of pharmaceuticals, steroid hormones, and endocrine-disrupting personal care products in wastewater and the recipient river water of the Pearl River Delta, South China. J Environ Monit 2011;13(4):871–8.
Yu K, Li B, Zhang T. Direct rapid analysis of multiple PPCPs in municipal wastewater using ultrahigh performance liquid chromatography-tandem mass spectrometry without SPE pre-concentration. Anal Chim Acta 2012;738:59–68.
Yusa V, Ye X, Calafat AM. Methods for the determination of biomarkers of exposure to emerging pollutants in human specimens. TrAC Trends Anal Chem 2012;38:129–42.
Zhang H. The orientation of water quality variation from the metropolis river – Huangpu River, Shanghai. Environ Monit Assess 2007;127(1–3):429–34.
Zhang S, et al. Simultaneous quantification of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and pharmaceuticals and personal care products (PPCPs) in Mississippi river water, in New Orleans, Louisiana, USA. Chemosphere 2007;66(6):1057–69.
Zhang D, et al. Contribution of different sulfamethoxazole species to their overall adsorption on functionalized carbon nanotubes. Environ Sci Technol 2010;44(10):3806–11.
Zhang X, et al. Levels of synthetic musk fragrances in human milk from three cities in the Yangtze River Delta in Eastern China. J Environ Sci 2011;23(6):983–90.
Zhang Y, et al. Determination and partitioning behavior of perfluoroalkyl carboxylic acids and perfluorooctanesulfonate in water and sediment from Dianchi Lake, China. Chemosphere 2012;88(11):1292–9.
Zheng BG, et al. Degradation of the emerging contaminant ibuprofen in aqueous solution by gamma irradiation. Desalination 2011;276(1–3):379–85.
Zheng Q, et al. Occurrence and distribution of antibiotics in the Beibu Gulf, China: Impacts of river discharge and aquaculture activities. Mar Environ Res 2012;78:26–33.
Zhou XF, et al. A preliminary study on the occurrence and behavior of carbamazepine (CBZ) in aquatic environment of Yangtze River Delta, China. Environ Monit Assess 2011;173(1–4):45–53.