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EMERGING CONTAMINANTS: A TUTORIAL MINI-REVIEW

N.S. THOMAIDIS*
A.G. ASIMAKOPOULOS
A.A. BLETSOU

Laboratory of Analytical Chemistry, Department of Chemistry
University of Athens, Panepistimiopolis - Zografou
15771 Athens, Greece

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*to whom all correspondence should be addressed:
e-mail: ntho@chem.uoa.gr

ABSTRACT
Nowadays, the scientific community has focused and prioritised research on “emerging pollutants”. The term “emerging pollutants” stands for the substances that are released in the environment for which currently no regulations are established for their environmental monitoring. Their occurrence is reported worldwide in a range of aquatic environments, such as lakes, rivers, freshwater catchments, estuaries, reservoirs and marine waters. Nevertheless, due to their large number (ranging in an order of thousands), only few of these compounds are toxicologically evaluated. Published data concerning occurrence and potential toxicological effects is limited. The contamination source of the aquatic environment is mainly the effluents from the sewage treatment plants (STPs). Reliable methods are available for residue analysis of these pollutants down to low ng L^{-1} levels. However, an urgent need is highlighted for the investigation (primarily in environmental media and following in biological ones) of the toxicity and transformation pathways of all emerging pollutants. The aims of this mini-review are to briefly present: (a) the major classes of emerging pollutants; (b) the reasons why these substances constitute an environmental issue; and (c) developments and applications of environmental analysis in this field.

KEYWORDS: Emerging Pollutants, wastewater, sewage treatment plants.

1. INTRODUCTION

Overwhelming evidence has shown that “new” xenobiotic substances have been produced over the last decade and nowadays are ubiquitous in the aquatic environment. These substances, referring to them as “emerging pollutants”, include a wide array of different compounds (as well as metabolites and transformation products - collectively referred also as degradates), can be detected with highly sensitive analytical methodologies in levels of parts per trillion (ppt), even in the most complex environmental matrices, such as sludge. Because of the vast number of possible compounds, many studies have occurred in different classes of emerging pollutants, according to priority lists established, taking into account consumption, predicted environmental concentrations, as well as ecotoxicological, pharmacological and physicochemical data. However their environmental impact (ecotoxicological and possible health risks for human) that is associated with their occurrence is still unknown. Although the reported concentrations are generally low, questions have been raised over the potential impacts of emerging pollutants in the environment on human and animal health after long-term exposure. Additionally, the extent in which the current water and wastewater treatment infrastructures can effectively remove these compounds is also, in great extent, an unknown parameter (Oulton *et al.*, 2010). The inefficient removal poses a serious environmental problem. Thus, it is a topic of growing interest from both research and regulatory perspectives.

2. EMERGING POLLUTANTS

As emerging pollutants are characterized the following wide range of substances: pharmaceuticals and personal care products (PPCPs), illicit drugs and drug of abuse, hormones and steroids, benzothiazoles, benzotriazoles, polychlorinated naphthalenes (PCNs), perfluorochemicals (PFCs), polychlorinated alkanes (PCAs), polydimethylsiloxanes (PDMSs), synthetic musks, quaternary

ammonium compounds (QACs), bisphenol A (BPA), triclosan (TCS), triclocarban (TCC), as well as polar pesticides, veterinary products, industrial compounds/by-products, food additives and engineered nano-materials (Lapworth *et al.*, 2012). Useful conclusions have been reached from research, which progresses rapidly, upon these substances that are briefly presented further below.

2.1. Pharmaceutical and personal care products – illicit drugs

Pharmaceutical and personal care products (PPCPs) maintain chemical properties that can vary widely, usually containing a non-polar core with a polar functional moiety. Their transformation products may be environmentally persistent (Clarke and Smith, 2011; Fent *et al.* 2006). For instance, the environmental persistence of the main active metabolite of the blood lipid regulators (clofibrate, erofibrate and theofibrate), clofibric acid, is 21 years (Díaz-Cruz *et al.*, 2003). Furthermore, pharmaceuticals may have unpredicted and unknown side effects on different organisms, particularly after long-term exposure to low concentrations, as well as they may provoke bacterial resistance from the release of antibiotics to the environment. Additionally, the potential effects of metabolites, in organisms of the ecosystem, are still unknown (Hernando *et al.*, 2011). PPCPs and their metabolites are often referred to as ‘‘effluent-derived’’ contaminants, originally present in wastewater. Antibiotics can be structurally categorized into the following groups: sulfonamides (SA), fluoroquinolones (FQ), nitroimidazoles (NI), penicillins (PE), cephalosporins (CE), tetracyclines (TC) and macrolides (MA) (Clarke and Smith, 2011; Jury *et al.*, 2011). The chemical properties of every substance determine its behavior through the wastewater treatment, the mobility, persistence and even the bioavailability in the soil matrix (Clarke and Smith, 2011). All antibiotics, many other pharmaceuticals and PPCPs have the tendency to persist or to be only partially degraded during treatment or even to bypass treatment altogether via sewage overflows, therefore, contributing to their load in receiving waters, many of which serve as recreational and drinking water sources (Clarke and Smith, 2011; Hernando *et al.*, 2011; Oulton *et al.*, 2010; Reif *et al.*, 2011; Wells *et al.* 2010).

One the other hand, the use of illicit drugs has gained worldwide concern due to their significant adverse impacts on human health and wellbeing of the society. Illicit drugs are those whose non-medical use is prohibited by the international law, and mainly belong to the classes of opiates, cocaine, cannabis, amphetamines and their metabolites. The chemicals associated with these illegal laboratories including precursors and by-products as well as the synthesized drugs are often illegally buried in soil or public waste management facilities, or disposed of into sinks or toilets after which they enter the sewerage system. Research on illicit drugs has been conducted with results showing that the presence of these compounds have temporal patterns that could be used to track use, but also that many of these compounds can be attenuated by WWTPs. Removal of illicit drugs by wastewater treatment was generally greater than 50%, except in a WWTP that uses primary treatment (Bell *et al.*, 2011; Castiglioni *et al.*, 2011; Richarson, 2012).

2.2. Steroids

Natural endogenous (17β-estradiol, estrone, estriol) and synthetic steroids (17α-ethinyloestradiol, mestranol) are excreted by humans and WWTP effluent is the primary source of synthetic steroids entering the environment. Estrogenic activity in WWTP effluents has resulted in adverse effects on environmental biota. Natural and synthetic steroids are excreted from the human body as inactive polar conjugates, but are present in sewage influent and effluent as free, active steroids. Once released from the body conjugated estrogens undergo chemical or enzymatic dissociation in bacterial sludge and reform as active estrogens (Fan *et al.*, 2011).

2.3. Perfluorochemicals

Perfluorochemicals (PFCs) are a family of anthropogenic chemicals that have been used to make products resistant to heat, oil, stains, grease and water. PFCs are persistent and widely dispersed in the environment. They are chemically unusual compounds, in that they are both hydrophobic and lipophobic, and they contain one of the strongest chemical bonds (C-F) known. The human and environmental toxicological response to such exposure is not known, but could include, among others, endocrine disruption (Clarke and Smith, 2011; Martin *et al.*, 2010). The chemical structures of PFCs make them very resistant to degradation in the environment. The two most common groups of PFCs that are measured and detected in environmental matrices are perfluoroalkyl sulphonates (PFASs) with main representative compound perfluorooctane sulphonate (PFOS) and perfluoroalkyl carboxylates (PFACs), with main representative compound perfluorooctanoic acid (PFOA). PFASs

and PFACs are synthetic chemicals that do not occur naturally in the environment. Mass balance studies of PFCs at WWTP commonly report higher mass loadings of PFOA and PFOS in WWTP effluent compared to raw influent (Takagi *et al.*, 2011). This suggests that the degradation of other fluorinated organic compounds (i.e. fluoropolymers) into PFOA and PFOS may take place during wastewater treatment (Clarke and Smith, 2011). In addition, perfluorooctane sulphonamide (PFOSA) has been the most frequently detected derivative of a third class, perfluorinated sulphonamides, but interestingly enough was often found below detection limits (Martin *et al.*, 2010).

2.4. Siloxanes and musks

Siloxanes consist of a structural unit of alternating Si-O bond with organic side chains. They include cyclic and linear siloxanes and form a large group of chemicals with molecular weights from a few hundred to several hundred thousands. Siloxanes are widely used in consumer products, such as paints and cosmetics, as well as in medical products, because of their high thermal stability, smooth texture, physiologic inertness and lubricating properties. They are, in general, very persistent once released in the environment. In recent years, various studies pointed out that some siloxanes may have endocrine disrupting properties and effects on the reproduction, which may cause concern about their effect on humans and the environment (Sánchez-Brunete *et al.*, 2010; Lu *et al.*, 2011). PDMSs have been detected in environmental samples, such as surface water, sediments and fish tissue. Cyclic siloxanes were found at greater concentrations than linear siloxanes in sediment samples. However, the summed concentrations of linear siloxanes were higher than the summed concentrations of cyclic siloxanes in sludge samples (Zhang et.al, 2011). PDMSs have low ecological toxicity, which occurs at higher concentrations than those observed in the environment, and are not considered to pose an ecologically significant threat. PDMSs have very low water solubility and are primarily removed by sorption to solids during wastewater treatment. At least 94% of PDMSs are unchanged during wastewater treatment, because of high chemical and thermal stabilities. PDMSs are not toxic to wastewater microbial communities and do not affect treatment performance. PDMSs, not removed on the sludge solids, are present in wastewater treatment effluent as a component of the suspended solids. PDMSs degrade in the soil environment, as a result of abiotic processes rather than biodegradation, and have a half-life estimated to range from 4 to 28 days (Clarke and Smith, 2011).

Synthetic musks have been used since the 1930s as fragrances in a variety of domestic and industrial products, e.g., detergent, cosmetics, shampoo, perfume, food and cigarette additives. WWTP mass balance studies indicated important removal rates (Clara, et.al, 2011; Clarke and Smith, 2011). Musks are highly lipophilic, so they tend to accumulate in sediments, sludges, and biota.

2.5. Polybrominated diphenyl ethers - polychlorinated alkanes - Polychlorinated naphthalenes

Polybrominated diphenyl ethers (PBDEs) are a class of brominated flame retardants (BFRs) that were used in plastics, textiles, electronic circuitry, and other materials. There are 209 PBDE congeners. There is concern about their use, because of their widespread presence in the environment and in human and wildlife samples, as well as their presence in locations far from where they were produced or used.

The technical mixtures of polychlorinated alkanes (PCAs), often referred to as chlorinated paraffins (CPs), are a class of industrial chemicals, comprising of chlorinated straight-chain hydrocarbons. Trace levels may be present in treated waste effluent. PCAs are divided into three groups: short-chain PCAs (noted as sPCAs or SCCPs) comprising 10 to 13 carbon atoms, medium-chain PCAs (mPCAs or MCCPs) comprising 14 to 17 carbon atoms and long-chain PCAs (lPCAs or LCCPs) with 18 or more carbon atoms. The total number of possible congeners is unknown, but far exceeds 10,000. The concentrations of PCAs in sewage sludge, evidence of accumulation in human and environmental biota, as well as toxicity data indicate that further research is necessary to assess the risk to human health and the environment from the industrial use of this chemical group. Technical mixtures of polychlorinated naphthalenes (PCNs) have been used since the early 1900s as dielectric fluids, engine oil additives, electroplating masking compounds, wood preservatives, lubricants, and for dye production. They are also structurally similar and have similar physico-chemical properties. There are 75 PCN congeners, substituted with one to eight chlorine atoms per naphthalene

molecule. PCNs are ubiquitous environmental contaminants and several PCN congeners exhibit dioxin-like toxicity (Clarke and Smith, 2011).

2.6. Quaternary ammonium compounds

Quaternary ammonium compounds (QACs) are cationic surfactants. The molecules contain at least one hydrophobic hydrocarbon alkyl chain linked to a positively charged nitrogen atom. The other alkyl groups are typically short-chain substituent's such as methyl or benzyl groups. Domestic use of QACs is the primary source of these compounds entering WWTPs. Removal of QACs in wastewater treatment can also be attributed to biodegradation, where degradation rates are typically reported in days or hours. WWTP discharges can result in environmental contamination of marine sediments with QACs (Lara-Martin *et al.*, 2010; Clarke and Smith, 2011).

2.7. Triclosan – triclocarban - bisphenol A

TCS and TCC are antimicrobial agents widely used in personal care products, such as shampoos, soaps, deodorants, cosmetics, skin-care lotions and creams, mouth rinses, and toothpastes. Mass balance studies at WWTP show the incomplete removal of TCC and TCS during wastewater treatment. Bisphenol A is a plasticizer manufactured in high quantities and is used mainly as a monomer for the production of polycarbonate and epoxy resins, unsaturated polyester. WWTP mass balance studies have detected bisphenol A in raw water, sewage sludge and effluents. Significant reductions (up to 99%) during wastewater treatment have been reported and biodegradation is thought to be the principal removal mechanism (Stasinakis *et al.*, 2008; Clarke and Smith, 2011).

2.8. Artificial sweeteners

Sucralose and other artificial sweeteners have recently been identified as persistent emerging pollutants (Richardson and Ternes, 2011). Sucralose is a relatively new artificial sweetener. It may seem like an odd compound to include as an emerging contaminant, but it is now being found widely in environmental waters and is extremely persistent (half-life up to several years). Several research groups have reported measurements of sucralose in the environment (including river water, groundwater, and coastal waters), and research has expanded to include other artificial sweeteners, such as acesulfame, saccharin, cyclamate, and aspartame (Scheurer *et al.*, 2009; Richarson, 2012). Because of their recalcitrance to transformation, acesulfame and sucralose were viewed as an ideal marker for the detection of domestic wastewater in environmental waters, particularly groundwater (Buerge *et al*., 2009; Oppenheimer *et al*., 2011).

2.9. Benzotriazoles - benzothiazoles

Benzotriazoles are complexing agents that are widely used as anticorrosives. The two common forms, benzotriazole (1H-benzotriazole) and tolyltriazole (a mixture of 4- and 5-methyl-1H-benzotriazole), are soluble in water, resistant to biodegradation, and only partially removed in wastewater treatment (Weiss and Reemtsma, 2005; Richarson, 2012). Benzothiazoles are used as corrosion inhibitors, herbicides, antialgal agents, slimicides in paper and pulp industry, photosensitizers, constituents of azo dyes, in de-icing/anti-icing fluids, chemotherapeutics and fungicides in lumber and leather production (Ni *et al.*, 2008). The benzothiazoles removal efficiencies ranged from zero to up to 80% in the conventional WWTP (Matamoros *et al.*, 2010).

2.10. Nanomaterials

Nanomaterials are 1 to 100 nm in size and can have unique properties, including high strength, thermal stability, low permeability, and high conductivity. In the near future, nanomaterials are projected to be used in areas such as chemotherapy, drug delivery, and labeling of food pathogens. The chemical structures of nanomaterials are highly varied, including fullerenes, nanotubes, quantum dots, metal oxanes, TiO_2 nanoparticles (NPs), nanosilver, nanogold, and zerovalent iron NPs. Most nanomaterial research is centered on developing new uses for nanomaterials and new products with unique properties, but on the other side, there is also significant concern regarding nanomaterials as environmental contaminants. As such, nanomaterials are the focus of researches, under which fate, transport, and health effects are being evaluated (Richarson, 2012).

3. ANALYTICAL METHODOLOGY FOR THE DETERMINATION OF EMERGING POLLUTANTS IN WASTEWATER AND SLUDGE

3.1. Sample pretreatment

For the extraction of target analytes or/and further sample cleanup (e.g. sludge matrix), the majority of methods involve liquid-liquid extraction (LLE) or/and solid phase extraction (SPE). Solid phase extraction (SPE) is the most preferred technique since it presents the advantages of simplicity, reproducibility, and applicability. SPE is a good way to preconcentrate water samples prior to the final determination to decrease detection limits, if necessary (Buchberger, 2011). A number of other less common extraction techniques have been also reported, including automated solid phase extraction, on-line solid phase extraction, use of molecularly imprinted polymers (MIPs), stir bar sorptive extraction (SBSE), solid phase microextraction (SPME) and magnetic solid phase extraction through silica supported Fe_3O_4 nanoparticles (Moliner-Martínez *et al.*, 2011). These techniques present various advantages, like less contamination between samples, higher sample throughput, minimized consumption of solvents and less labour work (Díaz-Cruz *et al.*, 2003; Wu *et al.*, 2010; Richardson and Ternes, 2011; Matamoros *et al.*, 2012; Yao *et al.*, 2011).

3.2. Instrumental analysis

Both liquid (LC) and gas (GC) chromatography is used for the determination of emerging pollutants, depending on the polarity, volatility and thermal stability of the concerning compounds. Due to the polarity of most pharmaceuticals, either LC-MS (/MS), or GC-MS (/MS) combined with derivatization, is normally used for their determination (Wu *et al.*, 2010; Helbing *et al.* 2010; Richardson and Ternes, 2011; Hummel *et al.*, 2006). Several methodologies, all based on LC-MS/MS, have been reported to determine illicit drugs and their metabolites in aqueous matrices. Few analytical methods have been published so far for the determination of illicit drugs in sewage sludge samples (Baker and Kasprzyk-Hordern, 2011; Díaz-Cruz *et al.*, 2009). However, when analyzing highly contaminated samples, such as sewage sludge, a suppression of the electrospray ionization during LC-MS (/MS) analysis is likely to occur. Thus, to guarantee accurate and reproducible data, an appropriate surrogate standard has to be spiked prior to SPE enrichment (Ternes, 2001). Capillary electrophoresis (CE) is generally less sensitive than HPLC procedures, so that it is not recommended as a first choice for residue analysis in the environment. Nevertheless, it may be an interesting alternative because its separation selectivity can be orthogonal to that of HPLC and one should consider this technique in cases when results from HPLC should be confirmed by a second independent method (Richardson and Ternes, 2011). Microbiological assays have been widely used especially for the determination of drugs in biological samples, but they have not found application in the analysis of soil, sediments or sludge, probably because of their limited sensitivity and specificity (Díaz-Cruz *et al.*, 2003). Immunoanalytical techniques may be promising for trace analysis of organic pollutants in the environment, since they require only minor sample preparation, exhibit high sensitivity, and may be less expensive in comparison with instrumental analysis based on chromatography and mass spectrometry. Nevertheless, the selectivity of the antibody used in an immunoassay makes it unsuited for simultaneous determination of analytes of different chemical classes (Buchberger, 2011). Polychlorinated alkanes represent a difficult analytical problem, because of the complexity inherent in industrial mixtures (Rusina et. al., 2011). Several investigations have examined the fate of estrogens in WWTPs, however, few studies have measured the concentrations of estrogenic compounds in sludge due to unresolved analytical problems, such as inefficient selectivity and high limits of detection (Richardson and Ternes, 2011; Liu *et al.*, 2010). For the determination siloxanes and synthetic musks in wastewater and soil samples, the method of choice is gas chromatography-mass spectrometry (Sánchez-Brunete *et al.*, 2010; Lv *et al.*, 2010).

4. SOURCES, OCCURRENCE AND FATE

Sources of emerging pollutants in the environment that may eventually impact groundwater can be divided into point-sources and diffuse sources of pollution. Point-source pollution originates from discrete locations whose inputs into aquatic systems can often be defined in a spatially discrete manner. The spatial extent or plume of pollution is therefore generally more constrained. Important examples include industrial effluents, municipal sewage treatment plants and combined sewage-storm-water overflows, resource extraction, waste disposal sites and buried septic tanks. Diffuse

pollution, in contrast, originates from poorly defined, diffuse sources that typically occur over broad geographical scales. Examples of diffuse source pollution include agricultural runoff from bio-solids and manure sources, storm-water and urban runoff, leakage from reticulated urban sewerage systems and diffuse aerial deposition.

While it is clear from literature review that the vast majority of groundwater resources do not contain emerging pollutants in concentrations that would be considered toxic and/or harmful due to natural attenuation and dilution mechanisms, there is a large variety of compounds found in groundwater, and in some cases their concentrations are significant (>100 ng L^{-1}). The combined toxicity of multiple contaminants is not well understood. In addition, there are a number of specific pollutants that have a global footprint, and are frequently detected in groundwater resources.

The most frequently reported group of compounds were pharmaceuticals, including analgesics, anti-inflammatory drugs, antibiotics, anti-epileptics (carbamazepine) and barbiturates (primidone). Two phenolic compounds (bisphenol A and nonylphenol (NP), both known endocrine disruptors), a flame retardant (tri(2- chloroethyl) phosphate) and the musk galaxolide were among the most frequently reported compounds (Richarson, 2012).

Diuretics, blood lipid regulators, beta blockers, analgesics, antibiotics and fragrances are also detected frequently in WWTP samples (Teijon *et al.*, 2010). Numerous pharmaceuticals, including carbamazepine, clofibric acid, diclofenac, fenofibric acid, gemfibrozil, and naproxen were ubiquitous in German sewage treatment plant effluent and river waters (Murray *et al.* 2010). The surface waters of the metropolitan area of Madrid are reported to be contaminated by pharmaceuticals. Carbamazepine concentrations in the rivers of Madrid agree well with predictions for Spain, as well as with high values found in other geographical areas (Alonso *et al.*, 2010). The presence of 'free' estrogens in WWTP effluents and receiving waters is commonly reported, demonstrating that the conversion of estrogen metabolites into active forms occurs somewhere between the domestic discharge and WWTP outlet (Clarke and Smith, 2011). Benzotriazole, caffeine, carbamazepine, tolyltriazole, and nonylphenoxy acetic acid (NPE1C) were the most frequently detected persistent organic pollutants in European river waters (Loos *et al.*, 2009). Endocrine disruption compounds (EDCs), coprostanol, N,N-diethyltoluamide (DEET), caffeine and triclosan were among the most frequently detected organic wastewater contaminants in U.S. streams. DEET, Bisphenol A (BPA), tri(2-chloroethyl) phosphate, and sulfamethoxazole were among the most frequently detected organic wastewater contaminants in U.S. groundwater (Murray *et al.* 2010). Accumulation of PFCs has been detected in ocean animals, such as birds and mammals, and in human tissues throughout the world (Clarke and Smith, 2011). The occurrence of synthetic musks in sewage sludge have been reported from Switzerland, Germany, Spain, UK, China and Hong Kong (Clarke and Smith, 2011). It should be noted, that effluent concentrations reported worldwide vary, probably due to differences in the regional use of the emerging contaminants and the efficiency of the wastewater treatments (Pal *et al.*, 2010).The fate of any given contaminant in the subsurface environment will depend upon both its physicochemical properties, such as its solubility in water, K_{ow} and D_{ow} and other environmental characteristics. Indeed, the contaminant properties as well as groundwater residence time, redox conditions and total loading will be important in determining presence and persistence in the subsurface and groundwater. The main processes controlling emerging pollutants during subsurface migration are sorption, mainly to organic matter and clay minerals, ion exchange in the soil and aquifer, and microbial degradation or transformations (Richarson, 2012).

REFERENCES

Alonso S.G., Catalá M., Maroto R.R., Gil J.L.R., De Miguel Á.G., Valcárcel Y., (2010), Pollution by psychoactive pharmaceuticals in the Rivers of Madrid metropolitan area (Spain), *Environ. Int.*, **36**, 195–201.

Baker D.R., Kasprzyk-Hordern B., (2011), Multi-residue analysis of drugs of abuse in wastewater and surface water by solid-phase extraction and liquid chromatography–positive electrospray ionisation tandem mass spectrometry, *J. Chromatogr*. A, **1218**, 1620–1631.

Bell K.Y., Wells,M.J.M., Traexler K.A., Pellegrin M., Morse A., Bandy J., (2011), Emerging Pollutants, *Water Environ. Res*., **83**, 1906-1984.

Buchberger W.W., (2011), Current approaches to trace analysis of pharmaceuticals and personal care products in the environment, *J. Chromatogr. A*, **1218**, 603–618.

Buerge I.J., Buser H.-R., Kahle M., Muller M.D., Poiger T., (2009), Ubiquitous Occurrence of the Artificial Sweetener Acesulfame in the Aquatic Environment: An Ideal Chemical Marker of Domestic Wastewater in Groundwater, *Environ. Sci. Technol.*, **43**, 4381-4385.

Castiglioni S., Zuccato E., Fanelli R. (2011), Illicit drugs in the environment, John Wiley & Sons, New Jersey.

Clara M., Gans O., Windhofer G., Krenn U., Hartl W., Braun K., Scharf S., Scheffknecht C., (2011), Occurrence of polycyclic musks in wastewater and receiving water bodies and fate during wastewater treatment, *Chemosphere*, **82**, 1116–1123.

Clarke B.O., Smith S.R., (2011), Review of 'emerging' organic contaminants in biosolids and assessment of international research priorities for the agricultural use of biosolids, *Environ. Int*., **37**, 226–247.

Díaz-Cruz M.S., de Alda M.J.L., Barceló D., (2003), Environmental behavior and analysis of veterinary and human drugs in soils, sediments and sludge, *Trends Anal. Chem.-TrAC*., **22**, 340-351.

Díaz-Cruz M.S., García-Galán M.J., Guerra P., Jelic A., Postigo C., Eljarrat E., Farré M., de Alda M.J.L., Petrovic M., Barcelo D., (2009), Analysis of selected emerging contaminants in sewage sludge, *Trends Anal. Chem.-TrAC*., **28**, 1263-1275.

Helbing D.E., Hollender J., Kohler P.E., Singer H., Fenner K., (2010), High throughput identification of microbial transformation products of organic micropollutants, *Environ. Sci. Technol*., **44**, 6621–6627.

Hernando M.D., Rodríguez A., Vaquero J.J., Fernández-Alba A.R., García E., (2011), Environmental risk assessment of emerging pollutants in water: Approaches under horizontal and vertical EU legislation, *Crit. Rev. Environ. Sci. Technol*., **41**, 699-731.

Hummel D., Löffler G., Fink Ternes T.A., (2006), Simultaneous determination of psychoactive drugs and their metabolites in aqueous matrices by liquid chromatography mass spectrometry*, Environ. Sci. Technol*., **40**, 7321-7328.

Fan Zh., Wu S., Chang H., Hu J., (2011), Behaviors of glucocorticoids, androgens and progestogens in a municipal sewage treatment plant: comparison to estrogens, *Environ. Sci. Technol.* **45**, 2725–2733.

Fent K., Weston A.A., Caminada D., (2006), Ecotoxicology of human pharmaceuticals, *Aquat. Toxicol.*, **76**, 122–159.

Jury K.L., Khan S.J., Vancov T., Stuetz R.M., Ashbolt N.J., (2011), Are sewage treatment plants promoting antibiotic resistance?, *Crit. Rev. Environ. Sci. Technol*., **41**, 243-270.

Lapworth D.J., Baran N., Stuart M.E., Ward R.S., (2012), Emerging organic contaminants in groundwater: A review of sources, fate and occurrence, *Environ. Pollut*., **163**, 287-303.

Lara-Martin P., Li X., Bopp R., Brownawell B.J., (2010), Occurrence of alkyltrimethylammonium compounds in urban estuarine sediments: behentrimonium as a new emerging contaminant, *Environ. Sci. Technol*., **44**, 7569–7575.

Liu Z., Kanjo Y., Mizutani S., (2010), A review of phytoestrogens: Their occurrence and fate in the environment, *Water Res*., **44**, 567-577.

Loos R., Gawlik B. M., Locoro G., Rimaviciute E., Contini S., Bidoglio G., (2009), EU-wide survey of polar organic persistent pollutants in European river waters, *Environ. Poll.*, 157, 561-568.

Lu Y., Yuan T., Wang W., Kannan K., (2011), Concentrations and assessment of exposure to siloxanes and synthetic musks in personal care products from China, *Environ. Pollut*., **159,** 3522-3528.

Lv Y., Yuan T., Hu J., Wang W., (2010), Seasonal occurrence and behavior of synthetic musks (SMs) during wastewater treatment process in Shanghai, China, *Sci. Tot. Environ.*, **408**, 4170–4176.

Martin J.W., Asher B.J., Beesoon S., Benskin J.P., Ross M.S., (2010), PFOS or PreFOS? Are perfluorooctane sulfonate precursors (PreFOS) important determinants of human and environmental perfluorooctane sulfonate (PFOS) exposure?, *J. Environ. Monit.*, **12**, 1979–2004.

Matamoros V., Jover E., Bayona J.M., (2010), Occurrence and fate of benzothiazoles and benzotriazoles in constructed wetlands, *Water Sci. Technol.– WST.*, **61**, 191-198.

Matamoros V., Calderón-Preciado D., Domínguez C., Bayona J.M., (2012), Analytical procedures for the determination of emerging organic contaminants in plant material: A review, *Anal. Chim. Acta,* **722**, 8-20.

Moliner-Martínez Y., Ribera A., Coronado E., Campins-Falco P., (2011), Preconcentration of emerging contaminants in environmental water samples by using silica supported Fe_3O_4 magnetic nanoparticles for improving mass detection in capillary liquid chromatography, *J. Chromatogr.* A, **1218**, 2276–2283.

Murray K.E., Thomas S.M., Bodour A.A., (2010), Prioritizing research for trace pollutants and emerging contaminants in the freshwater environment, *Environ. Pollut*., **158**, 3462-3471.

Ni H.-G., Lu F.-H., Luo X.-L., Tian H. Y., Zeng E. Y., (2008), Occurrence, Phase Distribution, and Mass Loadings of Benzothiazoles in Riverine Runoff of the Pearl River Delta, China, *Environ. Sci. Technol.*, **42**, 1892- 1897.

Oppenheimer J., Eaton A., Badruzzaman M., Haghani A. W., Jacangelo J. G., (2011), Occurrence and suitability of sucralose as an indicator compound of wastewater loading to surface waters in rbanized regions, *Water Res.*, **45**, 4019-4027.

Oulton R.L., Kohn,T., Cwiertny D.M., (2010), Pharmaceuticals and personal care products in effluent matrices: A survey of transformation and removal during wastewater treatment and implications for wastewater management, *J. Environ. Monit.*, **12**, 1956–1978.

Pal A., Gin K.Y.-H., Lin A.Y.-C., Reinhard M., (2010), Impacts of emerging organic contaminants on freshwater resources: Review of recent occurrences, sources, fate and effects, *Sci. Tot. Environ*., **408**, 6062–6069.

Reif R., Santos A., Judd S.J., Lema J.M., Omil F., (2011), Occurrence and fate of pharmaceutical and personal care products in a sewage treatment works, *J. Environ. Monit.*, **13**, 137-144.

Richardson S.D., Ternes T.A., (2011) Water Analysis: Emerging Contaminants and Current Issues, *Anal. Chem.,* **83**, 4614–4648.

Richardson S.D., (2012), Environmental Mass Spectrometry: Emerging Contaminants and Current Issues, *Anal. Chem*., **84**, 747–778.

Rusina T.P., Korytar P., de Boer J., (2011), Comparison of quantification methods for the analysis of polychlorinated alkanes using electron capture negative ionization mass spectrometry, *Int. J. Environ. Anal Chem*., **91**, 319-332.

Sánchez-Brunete C., Miguel E., Albero B., Tadeo J.L., (2010), Determination of cyclic and linear siloxanes in soil samples by ultrasonic-assisted extraction and gas chromatography – mass spectrometry, *J. Chromatogr. A*, **1217**, 7024-7030.

Scheurer M., Brauch H.-J., Lange F. T., (2009) Analysis and occurrence of seven artificial sweeteners in German waste water and surface water and in soil aquifer treatment (SAT), *Anal. Bioanal. Chem.*, **394**, 1585–1594.

Stasinakis A.S., Gatidou G., Mamais D., Thomaidis N.S., Lekkas T.D., (2008), Occurrence and fate of endocrine disrupters in Greek sewage treatment plants, *Water Res*., **42**, 1796-1804.

Takagi S., Adachi F., Miyano K., Koizumi Y., Tanaka H., Watanabe I., Tanabe S., Kannan K., (2011), Fate of perfluorooctanesulfonate and perfluorooctanoate in drinking water treatment processes, *Water Res.*, **45**, 3925-3932.

Teijon G., Candela L., Tamoh K., Molina-Díaz A., Fernández-Alba A.R., (2010), Occurrence of emerging contaminants, priority substances (2008/105/CE) and heavy metals in treated wastewater and groundwater at Depurbaix facility (Barcelona, Spain), *Sci. Total Environ*. **408**, 3584–3595.

Ternes T.A., (2001), Analytical methods for the determination of pharmaceuticals in aqueous environmental samples, *Trends Anal. Chem.-TrAC*, **20**, 419-434.

Weiss S., Reemtsma T., (2005), Determination of Benzotriazole Corrosion Inhibitors from Aqueous Environmental Samples by Liquid Chromatography-Electrospray Ionization-Tandem Mass Spectrometry, *Anal. Chem.*, **77**, 7415- 7420.

Wells M.J.M., Bell K.Y., Traexler K.A., Pellegrin M.-L., (2010), Emerging Pollutants, *Water Environ. Res.*, **82**, 2095-2170.

Wu J., Zhang L., Yang Z., (2010), A review on the analysis of emerging contaminants in aquatic environment, *Crit. Rev. Anal. Chem*., **40**, 234-245.

Yao, C., Li, T., Twu, P., Pitner, W.R., Anderson J.L., (2011), Selective extraction of emerging contaminants from water samples by dispersive liquid–liquid microextraction using functionalized ionic liquids, *J. Chromatogr.* A, **1218**, 1556–1566.

Zhang Z., Qi H., Ren N., Li Y., Gao D., Kannan K., (2011), Survey of Cyclic and Linear Siloxanes in Sediment from the Songhua River and in Sewage Sludge from Wastewater Treatment Plants, Northeastern China, *Arch. Environ. Contam. Toxicol.*, **60**, 204–211.