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Monitoring of selected priority and emerging contaminants in the Guadalquivir River and other related surface waters in the province of Jaén, South East Spain

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HIGHLIGHTS

- 373 pollutants monitored in surface waters from the province of Jaén (S.E. Spain)
- Combination of an experimental LC–TOFMS database together with a GC–MS/MS method
- 83 samples analyzed from different water bodies (rivers, reservoirs and wetlands)
- Concentrations found of studied priority compounds were below the WFD standards.
- Olive grove pesticides and ubiquitous pharmaceuticals were the main species found.

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ABSTRACT

The province of Jaén counts with four natural parks, numerous rivers, reservoirs and wetlands; moreover, it is probably the region with higher olive oil production in the world, which makes this zone a proper target to be studied based on the European Water Framework Directive 2000/60/CE. The aim of this survey is to monitor a total number of 373 compounds belonging to different families (pesticides, PAHs, nitrosamines, drugs of abuse, pharmaceuticals and life-style compounds) in surface waters located at different points of the province of Jaén. Among these compounds some priority organic substances (regulated by the EU Directive 2008/105/EC) and pollutants of emerging concern (not regulated yet) can be found. A liquid chromatography electrospray time-of-flight mass spectrometry (LC–TOFMS) method covering 340 compounds was developed and applied, together with a gas chromatography triple–quadrupole mass spectrometry (GC–MS/MS) method which enabled the analysis of 63 organic contaminants (30 of these compounds are analyzed by LC–TOFMS as well). From April 2009 to November 2010 a total of 83 surface water samples were collected (rivers, reservoirs and wetlands). In this period numerous organic contaminants were detected, most of them at the ng L^{-1} level. The most frequently priority substances found were chlorpyrifos ethyl, diuron and hexachlorobenzene. Within the other groups, the most frequently detected compounds were: terbuthylazine, oxyfluorfen, desethyl terbuthylazine, diphenylamine (pesticide family); fluorene, phenanthrene, pyrene (PAHs group), codeine, paracetamol (pharmaceuticals compounds) and caffeine, nicotine (life-style compounds). As is could be expected, the total concentration of emerging contaminants is distinctly larger than that of priority pollutants, highlighting the importance of continuing with the study of their presence, fate and effects in aquatic environments. However, concentration levels (at the ng per liter level) are low in general for both kinds of contaminants which minimizes the possible harmful effect on the environment.

1. Introduction

Water quality is an important issue in the European Union. Particularly, there is a growing concern related to the presence of emerging and priority substances in surface water. For this reason, the European Union Water Framework Directive (WFD) (Directive 2000/60/EC) was set, committing European Union member states to achieve good ecological and chemical status of all water bodies. The WFD first established a list of 33 priority compounds (Decision 2455/2001 EC) — that represented a significant risk to or via the aquatic environment — to be monitored in water in order to evaluate their levels. Environmental Quality Standards (EQSs) have been set to control the concentration levels of these compounds in surface waters (Directive 2008/105/EC). On the

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basis of these EQSs, member states have to establish monitoring programs in order to have a comprehensive overview of water status within each river basin district. Additionally, member states have to identify their river basin specific pollutants, which will be the basis of further updates of the list of priority substances. Recently, the European Union has approved a directive (Directive 2013/39/EU) that increases the number or priority substances up to 45, including aclonifen, cypermethrin, heptachlor and terbutryn, among others.

The hazardous nature of priority pollutants is caused by their toxicity in combination with high chemical and biological stability, and a high lipophilicity. They accumulate in the adipose tissues of fishes, wildlife and humans through dietary and non-dietary routes (Barron, 1990; Kelly et al., 2004). A major part these contaminants that are released into aquatic environments will be incorporated in sediments (Landrum and Robbins, 1990). These sediments might later act as the major source of contaminants to water and biota. Hence, different studies have been undertaken to measure the occurrence and significance of priority substances in different types of water samples, such as wastewater (Barco-Bonilla et al., 2013; Martí et al., 2011; Pitarch et al., 2007; Robles-Molina et al., 2010, 2013; Sánchez-Avila et al., 2009), drinking water (Auersperger et al., 2005; León et al., 2006; Tillner et al., 2013; Wu et al., 2011) and surface water (Erger et al., 2012; Esteban et al., 2014; Navarro et al., 2010; Olujimi et al., 2012; Tahboub et al., 2005; Vorkamp et al., 2014). In general, the concentration of the detected compounds in these reports was at the ng L^{-1} level.

However, the focus for water pollution research has recently been shifted from the conventional organic priority pollutants to the so-called emerging contaminants, many of them not being regulated yet. They include pharmaceuticals, personal care products and disinfectants, among others. It is not necessary for these contaminants to persist in the environment to cause negative effects since their high transformation/removal rates can be compensated by their continuous introduction into the environment (Daughton, 2004; Petrović et al., 2003). Pharmaceuticals and personal care products (PPCPs) enter surface water mainly through insufficiently treated wastewater effluent. The level of their concentration and fate in the aqueous environment varied and depended on several parameters such as geographical position, effectiveness of wastewater treatment, proximity to wastewater plants and meteorological conditions, mainly rainfall (Kasprzyk-Hordern et al., 2008). For these reasons, several surveys of their appearance in the environment have been carried out in the last years (Estévez et al., 2012; Gracia-Lor et al., 2012; Gros et al., 2012; Huerta-Fontela et al., 2010; Martínez Bueno et al., 2012; Petrović et al., 2014; Reemtsma et al., 2013). From these studies, the most comprehensive in terms of sampling area was carried out by the Joint Research Centre — Institute for Environment and Sustainability (JRC-IES), monitoring 35 selected polar organic pollutants in 122 samples of European rivers (Loos et al., 2009).

The most widely used analytical methodologies for the analysis of priority and emerging contaminants in environmental waters are based on solid phase extraction (SPE) followed by either liquid chromatography coupled to mass spectrometry (LC–MS) or gas chromatography coupled to mass spectrometry (GC–MS) (Gómez et al., 2009; Petrovic et al., 2010; Richardson, 2012). The analysis of selected contaminants by tandem mass spectrometry (MS/MS) is the most common approach. However, to characterize the chemical contamination associated with a river basin, it is very convenient the development of screening methods based on high sensitive full scan acquisition, which permits retrospective analysis and detection of "non-target" or unexpected compounds. To this aim, high resolution mass analyzers, such as time-of-flight or orbitrap (LC–TOFMS) have the ability to record an unlimited number of compounds because of operating in full-scan mode, being this approach really convenient for the development of screening strategies based on using accurate-mass databases (De Castro et al., 2012; Díaz et al., 2012; Gómez-Ramos et al., 2011; Hug et al., 2014; K'oreje et al., 2012; Nurmi and Pellinen, 2011).

With a length of 657 km, the Guadalquivir River is one of the most important rivers in Spain, it flows southwest through the region of Andalusia, with a drainage area of 57,527 km^2, affecting population regions of more than 4 million inhabitants. In order to evaluate the organic contamination of this river, several studies have been carried out to monitor pesticides (Belmonte Vega et al., 2005; Campo et al., 2013; Masiá et al., 2013) or pharmaceuticals (Martín et al., 2011; López-Serna et al., 2013), the later often related to sewage treatment plants (STP) discharges. In the present work we perform a study the occurrence of 373 organic compounds, comprising a LC–TOFMS database (340 compounds) and a GC–MS/MS method (63 compounds). The target area covers surface waters related to the beginning of the Guadalquivir River basin in the province of Jaen, which is highly affected by olive harvesting, and also by wastewater discharges.

2. Material and methods

2.1. Chemical and reagents

The list of organic compounds studied is included in Table 1. Standards were purchased from Sigma-Aldrich (Steinheim, Germany) and Dr. Ehrenstofer (Augsburg, Germany). Ethyl acetate and n-hexane were obtained from Riedel-de Häen (Seelze, Germany), methanol and acetonitrile from Sigma-Aldrich (Steinheim, Germany) and formic acid from Fluka (Madrid, Spain). Anhydrous sodium sulfate and sodium chloride were purchased from J.T. Baker (Deventer, Holland) and sulfuric acid from Panreac (Castellar del Valles, Spain). All of them were provided with the adequate purity. Individual stock standard solutions for LC–TOFMS were prepared at a concentration level of 1000 μg mL^{-1} by dissolving the analytes in methanol and mixtures of acetonitrile and methanol depending on the compound solubility. For GC–MS/MS analysis individual stock standard solutions were prepared in n-hexane or ethyl acetate and mixtures containing both solvents, at a concentration level of 1000 μg mL^{-1}. The working standard solutions with the different mixtures of compounds were prepared by appropriate dilutions of the stock solutions with methanol or n-hexane for LC and GC injection respectively.

2.2. Analytes selected

Analytes included in this study were selected taking into account the agricultural activity of sampling area, the European list of priority substances (Directive 2013/39/EU), the United Stated Environmental Protection Agency methods for monitoring drinking water (www.epa.gov/safewater/methods/analyticalmethods.html) and published literature (Hernández et al., 2007; Kolpin et al., 2002; Martínez-Bueno et al., 2007; Postigo et al., 2008). They comprise a group of 373 organic pollutants belonging to different compound categories: pharmaceuticals, life-style compounds (LS), drugs of abuse, pesticides, nitrosamines, polycyclic aromatic hydrocarbons (PAHs) and some of their more relevant metabolites. Among the pharmaceuticals, there are representatives of different therapeutical groups, such as *analgesics/anti-inflammatories* (paracetamol, indomethacine, codeine, mefenamic acid, naproxen, ibuprofen, diclofenac, ketoprofen), *antibiotics* (metronidazole, sulfamethoxazole, trimethoprim, cefotaxime, ofloxacin, erythromycin), *lipid regulators* (fenofibrate, bezafibrate, gemfibrozil), *β-blockers* (atenolol, pindolol, timolol), *antiepileptic/psychiatrics* (carbamazepine, fluoxetine), *ulcer healings* (ranitidine), *diuretics* (furosemide, hydrochlorothiazide), and *bronchodilatadors* (salbutamol). Because of their relevance, metabolites such as, clofibric acid and fenofibric acid were also included. Regarding drugs of abuse selected, they comprise *stimulants* (cocaine, ephedrine, amphetamine and some of the compounds that are referred as amphetamine family (3,4-Methylenedioxyamphetamine — MDA-, 3,4-Methylenedioxy-N-methylamphetamine — MDMA-)), *opiate analgesic drugs* (methadone, morphine, heroine) *cannabinoids* (cannabidiol, delta-9-tetrahydrocannabinol (Δ-9-THC)) and several metabolites from