Monitoring the complex occurrence of pesticides in the Llobregat basin, natural and drinking waters in Barcelona metropolitan area (Catalonia, NE Spain) by a validated multi-residue online analytical method

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Abstract

The European Directive 98/83/CE legislates the presence of pesticides in drinking water. However, apart from for a few compounds, nothing is said about the amounts of pesticides that should be monitored. Nevertheless, water companies need to go beyond the strict accomplishment of the legislation and find out the amount of pesticide contamination in all sources of water involved in the consumption of tap water in order to manage the hazard assessment, and to guarantee safe drinking water to all the population.

Until now, monitoring programs have been usually focused on compounds that are chosen according to expert knowledge, or to previous monitoring campaigns, or analytical feasibility. Modern insecticides, fungicides, new priority pollutants or transformation products are seldomly included in monitoring programs, although their assessment would be highly desirable. The aim of this work was to develop an analytical multi-residue method for *circa* 100 compounds. The method analyses those previously monitored compounds in Barcelona city and its metropolitan area (triazines, carbamates, organophosphorated, phenoxy acid and phenylurea families), as well as many emerging pesticides (neonicotinoids, fluroxypyr, carbendazim, metalaxyl, propiconazole and sulcotrione among others) listed in the Water Framework Directive (WFD) and in the latest European monitoring programs, and some selected transformation products. A fast UHPLC-MS/MS method, which includes 0.75 mL of on-line sample extraction has been developed for natural and treated waters. Linearity, trueness, precision, uncertainty and performance of the method were calculated according to ISO/IEC 17025, obtaining limits of quantification in the range of 5-25 ng/L for most of the monitored compounds. A through monitoring campaign over natural and treated waters in the Barcelona metropolitan area was carried out during 2016-2017. Results show that pesticide contamination at the low stretch of Llobregat River and in its aquifer, which supplies raw water to Barcelona's drinking water treatment plants (DWTPs), is severe due to Anoia River and Rubí Creek contributions, which show maximum concentrations in the range of few µg/L for some compounds. However, the efficiency of advanced treatments in the DWTPs involved in drinking water production in the Barcelona metropolitan area allows the complete removal of pesticides in DWTP1, and an important decrease of the concentration levels of a number of regulated compounds in the rest of DWTPs.

Keywords

Llobregat River, Ter River, water analysis, pesticides monitoring, risk assessment, water treatment

Highlights

- Intensive monitoring data from the Llobregat River basin (NE Spain) and drinking water of Barcelona metropolitan area during two years.
- Identification of non-previously reported pesticides and metabolites in natural waters.
- Ocurrence of pesticide in drinking water of 3 milion people and risk assessment reavaluation after analytical results.
- High levels of pesticide pollution for some analytes in the sources of drinking wàter, but high efficiency in its removal in the treatment processes involved.
- Validation of a novel on-line extraction method according EN ISO/IEC 17025.

1. Introduction

No other chemical family is probably as closely monitored as pesticides, and guidelines and directives exist in most countries for food and drinking water. Carbamates, organophosphorus compounds, pyretroids, sulfonylureas or triazines are the most important groups. Despite the intense research in this field, and the prohibition or restriction in the use of some pesticides, new compounds and groups of compounds such as neonicotinoids (Starner and Goh, 2012) or azoles (Kahle et al., 2008) have been launched to the market.

Regulations are gradually introduced when toxicological data for biota or human health appears, to avoid its presence in the aquatic environment, and especially in water resources intended for drinking water consumption. While USA regulations in the Safe Drinking Water Act are set according to toxicological data, in Europe regulations (Directive (UE) 2015/1787) are set according to the precautionary principle (0.1 µg/L for individual compounds), and only individual parametric values exist for the most relevant compounds. The aquatic environment is considered in Europe a natural resource, and the European Union's Water Framework Directive (WFD) (Directive 2000/60/EC) was approved in order to protect it. There is also a regulated and regularly updated list (Directive 2013/39/CE) for priority compounds that need more occurrence data prior to authorize new standards, setting environmental quality standards (EQS), annual average (AA) and maximum allowable concentration (MAC). Also, in an issue published in 2013, there were 45 priority substances to be controlled, among which 24 were pesticides or biocides. Even so, the number of authorised active ingredients in pesticide formulations is still high (460 in 2016) (EU, 2016), and the pesticides sales market do not stop to increasing in Europe, particularly in Spain (Eurostat, 2015).

The presence of pesticides in the aquatic environment comes from the agriculture, urban, industrial and household usages. Several reports suggest that the amount of biocides used in non-agricultural uses is similar to those used in agricultural uses (Lassen et al., 2001; Stone et al., 2014). While pesticides reach the aquatic environment directly from the agricultural activity, the main inputs of pesticides in surface waters from urban and industrial usages are discharges of effluents from wastewater treatment plants (WWTPs). This is because, in general, secondary treatments of WWTPs do not properly remove this type of compounds (Barco-Bonilla et al., 2010; Campo et al., 2013; Kahle et al., 2008; Petrović et al., 2003; Singer et al., 2010). This is especially relevant in some geographical areas where water is a scarce and valuable asset and an efficient management of available water is needed, which should monitor its continuous presence because its high production, consumption and low dilution ratio of WWTPs' effluents. Intended to be used afterwards in waterworks for drinking water production, in this cases a common practice is the use of reclaimed water to restore river flows or injection into aquifers (Aggeli et al., 2009).

Metabolites or transformation products of pesticides are also present in the aquatic environment because many of them are polar and persistent (Jurado et al., 2012; Postigo et al., 2010). Their occurrence in the catchment of drinking water treatment plants (DWTPs) lays out a challenge in water treatment processes because they are difficult to remove due to their hydrophilicity, even for the most advanced treatments. The occurrence of some relevant metabolites in Europe led to the restriction in the use of certain pesticides (*e.g.* atrazine and dichlobenil). In addition, some studies showed their potential for subsequent highly toxic by-products in the DWTPs oxidative stages (Schmidt and Brauch, 2008).

Drinking water quality monitoring in Europe has been undergoing a change of strategy in recent years, shifting from the final product control to risk evaluation and management systems. In 2004, the World Health Organization (WHO, 2004) proposed the implementation of Water Safety Plans based on preventive risk management and critical points analysis which are the most effective means to consistently ensure the safety of final water in all steps in a drinking water supply system from catchment to consumption (Birkholz et al., 2014; Carriger and Rand, 2008; Köck-Schulmeyer et al., 2012; Palma et al., 2014; Silva et al., 2015). Special attention is needed to the presence of pesticides, biocides and metabolites in order to assess and manage the associated risks to human consumption water in drinking water, as well as any other source of raw water.

Monitoring programs allow better risk assessments for waterworks managers and to adopt the right preventive measures to improve the quality of final drinking water. Therefore, they should be as complete and smart as possible, and they should include all those compounds detected in previous screenings, as well as the emerging and new ones, taking into account as many variables as possible in the studied geographical area (market sales, typology of agriculture and industry, population and wastewater management…). However, the number of monitored compounds is usually very limited. Also, compounds are chosen according to their sanitary standards, and to previous monitoring programs and the probability to detect certain compounds, as well as the availability of the analytical instrumentation, and the need to manage an affordable list of compounds in routine analysis. Neverhteless, emerging contaminants or metabolites are seldomly monitored. Recent studies (Moschet et al., 2014; Reemtsma et al., 2013; Schreiner et al., 2016) disclosed as monitoring programs with a large amount of compounds can lead the occurrence of non-previously reported compounds in a certain geographical area, sometimes at relevant concentrations, and how the summation of total amount of pesticides can appreciably change the risk assessment associated to these samples.

In the last decades, the progressive development of triple quadrupole (Alder et al., 2006), time-of-flight (Ferrer and Thurman, 2007; Leendert et al., 2015) and more recently Orbitrap mass spectrometers and ionization techniques like ESI or API (Thurman et al., 2001) has been turning liquid chromatography (LC) coupled to mass spectrometry (MS) as the best method to analyse hydrophilic compounds (pKow<2) for most pesticides and metabolites. In addition, recent development of LC columns particle size below 2.5 µm allowed the progress from former high performance LC (HPLC) to ultra high performance LC (UHPLC) (Marín et al., 2009; Mezcua et al., 2006). Regardless instrumentation improvement, sample preparation is still usually needed and nowadays Solid Phase extraction (SPE) in combination with LC is the most applied technique for the extraction of pesticides residues from water. On-line SPE is considered an elegant alternative for the automatization, miniaturization, short time of analysis, improvement of reproducibility, accuracy and sensitivity of the extractive process (Kampioti et al., 2005; Postigo et al., 2010; Singer et al., 2010).

Drinking water in Barcelona city and in 23 other surrounding municipalities of its metropolitan area is served to almost 3 million consumers daily by Aigües de Barcelona-EMGCIA Co. for the last 150 years. This water company also manages one of the most complex waterworks of Europe (DWTP1) located in the final stretch of Llobregat River, which one of the most polluted and studied rivers by the Spanish scientific community (Sabater et al., 2012) due to its water scarcity, density of population and industrial development. The distribution net of drinking water is composed by 4500 kilometres of pipelines, 72 reservoirs and 8 different sources of water distributed in seven water supply zones. Because of this complex infrastructure and the need to properly and preventively manage the sanitary risk (Ganzer et al., 2011a; Ganzer et al., 2011b), an analytical effort is needed in order to study the occurrence of pollutants that could compromise a safe drinking water. Thus, the aim of this work is to develop an analytical multi-residue method for more than 100 compounds, including those previously monitored in Llobregat River basin (triazine, carbamate, organophosphorated, phenoxy acid and phenylurea groups), as well as some emerging pesticides from WFD (neonicotinoids, fluroxypyr, carbendazim, metalaxyl, propiconazole, sulcotrione among others), and a list of European monitoring programs and selected transformation products. A fast UHPLC-MS/MS method including on-line extraction of 0.75 mL of sample has been developed for natural and treated waters. Linearity, trueness, precision, uncertainty and performance of the method were calculated in agreement with EN ISO/IEC 17025 and EU recommendations (EU, 2002). The present method has been routinely used during 2016 and 2017 to intensively sample the Llobregat River basin and its tributaries and its groundwater aquifer. The same method has been used in other metropolitan sources that produce drinking water, as well as in the distribution water system in all water supply zones according to the European Drinking Water Directive. The method also allows the evaluation of the effectiveness of removal of these chemicals ain different DWTPs managed by our company.

2. Material and methods

2.1 Site description

2.1.1 Surface waters.

Barcelona metropolitan area has a drinking water demand for almost three million inhabitants, although its sources of water are scare because of its Mediterranean climate. Their main sources (Figure 1) are the Llobregat River (surface and groundwater) and the Ter River (52% and 24% respectively). Many European rivers have fairly constant flows >1500 m^3/s, but Mediterranean rivers are characterized by their low average flows with intermittently high flow peaks, such as Llobregat River (22 m^3/s of annual average flow but with a 2-5 m^3/s flow most of the days of the year, Figure S1) or Ter River (annual average flow of 27 m^3/s). Apart from the water scarcity, the management of drinking water in the Mediterranean area has some other extra difficulties, compared with other areas in Europe, such as the industrial impacts, the pollution, the wastewater management and the demand of a minimum ecological flow in the context of WFD. For these reasons, a good management of all possible sources of water in Barcelona metropolitan area is required. In this sense, some concrete measures have been taken, and we can mention the desalination sea water treatment plant (SWTP) (2.3 m^3/s maximum from up to 22.5% of Barcelona metropolitan area consumption if needed) which started operating in 2009, and the recovery of the aquifer of Besòs River for drinking water production (2.5% if needed) in the early 2000’s. Both measures are alternative and complementary supplies.

Llobregat River is 160 Km long and it flows from the north to the south from central Catalonia, finishing at a delta located in the Barcelona’s metropolitan area. Cardener and Anoia Rivers are its main tributaries. Cardener River has a low anthropogenic pollution impact over Llobregat River. Anoia River basin is at a very industrialized area where tannery industries and vineyard farming are the main spot of pesticide pollution. The Rubí Creek is another spot of industrial pollution. The final stretch of Llobregat River is densely populated and highly industrialized and the impact of around 30 WWTPs effluents along the river length (around 137 $Mm^3/year$ (Ginebreda et al., 2010)) influence the overall water cycle.

Ter River is 200 Km long and it flows far from Barcelona metropolitan area, from the north to the east of Catalonia, and it goes through an agricultural area. It has three reservoirs, and the 75% of river flow is diverted by a pipeline 56 Km long to a DWTP2 sited in Cardedeu, which serves drinking water to central Catalonia and to the Barcelona metropolitan area by another pipeline (80 km long).

A more detailed information about the sites descriptions can be found in the supporting information (SI).

2.1.2 Llobregat River aquifer.

In its final stretch, the aquifer of Llobregat River is 115 Km^2 wide and contains 100 Hm^3 of groundwater, which has been extensively used for water production for more than a century. At present, it contributes to 10% of drinking water consumption in Barcelona metropolitan area. The wells intended for water production are sited close to DWTP1. Groundwater extraction is performed in two areas, the main one comprises around 15 wells (samplings points gathered to GW-LLO-2, Figure 1) where water is transported to DWTP1 and blended with surface water at the sand filters (Figure 2).

2.1.3 Drinking Water Treatment Plants (DWTPs).

DWTP1 (7 m^3/s) is located in the last stretch of Llobregat River, before the discharge of bypass system of Anoia River, Rubí Creek and several industrial and urban wastewater effluents (see SI). After a conventional pretreatment (including clarification and sand filtration), the water is split between a conventional refining treatment including ozonation followed by a filtartion through granular activated carbon (GAC), and an advanced treatment line that uses membrane technology. Both conventional and advanced treatments of produced water are blended and the percentage of water production in both treatments is variable, and it depends on the quality of the raw water (Figure 2).

Three wells of Llobregat River aquifer (GW-LLO-1) from an area that was contaminated by chlorinated and non-chlorinated compounds in the 80's (Carrera et al., 2017; Guardiola et al., 1989; Martí and Ventura, 1997; Ventura et al., 1997) are used in DWTP4 (1 m^3/s if necessary). Previous elimination of volatile pollutants by air stripping and further chlorination drinking water is supplied to a concrete zone (<1% of Barcelona metropolitan area consumption) (Zone B2, see figure 3).

DWTP2 can produce up to 8 m^3/s of drinking water from the Ter River by conventional treatment (pre-chlorination, coagulation and sedimentation followed by filtering through GAC and a final disinfection using chlorine). Produced water is used to supply Barcelona Metropolitan area and to other areas nearby.

DWTP3 (4 m^3/s) is sited in the Llobregat River before the Anoia River confluence. After an initial removal of gravel and coarse sand, coagulation and sedimentation is done followed by disinfection with chlorine dioxide and the clarified water is driven by gravity through the open sand filters and followed by filtering through GAC. At this stage, 60% of water produced is separated and treated by an advanced treatment that uses electrodialysis reversal treatment technology (Valero et al., 2013).

Besòs River, the third closest river from Barcelona city (18 Km long and annual average flow of 4 m^3/s) stopped been used for human consumption in the 1950s due to its high contamination levels from industrial activities and the absence of wastewater management. However, the improvement of the raw water quality, thanks to several corrective measures applied, groundwater from this aquifer started being used in 2000s (<2% of Barcelona metropolitan area consumption if necessary). DWTP5 can produce 0.5 m^3/s from Besòs River groundwater by an advanced treatment membrane technology (nanofiltration and reverse osmosis) (Quintana et al., 2001; Radjenovic et al., 2008) and the produced water is blended with drinking water that comes from DWTP2.

Since 2009 SWTP located in the mouth of Llobregat River can produce up to 2 m3/s during drought periods. However, less than 20% of capacity is used during non-drought periods. Seawater is treated with a flocculation step, followed by a microfiltration and reverse osmosis. The resulting treated water is transported through a 12 Km long pipe to reservoir R1 (Figure 3).

2.1.4 Supply zones.

Figure 3 shows the Barcelona metropolitan area drinking water distribution system, where the four main reservoirs are indicated as R1, R2, R3 and R4. Until 2012 the water from Llobregat River came from reservoirs R1 and R2 and it was produced in DWTP1 and DWTP3 and it supplied treated water to the Western part of the Barcelona metropolitan area. Ter River water produced in DWTP2 supplied water to the Eastern part of Barcelona metropolitan area and it came from reservoir R3. The South of Barcelona metropolitan area drank water from a mixtures of treated water of both rivers. These rivers have different water qualities and salinity gives a characteristic salty taste to the water treated at Llobregat River waterworks. SWTP can be operated during long drought periods, but usually no more than 1% of water is therein produced and water is blended with water that comes from DWTP1 and DWTP3 in R1. Since 2012, a 12 Km long pipe is able to transport bidirectionally 4 m^3/s of water between R1 and R3 depending on the supply needs. Consequently, water from different origins is blended and different tap water qualities can be found in any place of Barcelona city. Both DWTP2 and DWTP3 serve drinking water to central Catalonia too. In fact, only a small part of this treated water is sent to the Barcelona metropolitan area distribution system.

According to the definition for "supply zone" stated in the Directive (UE) 2015/1787 –"a geographically defined area within which water intended for human consumption comes from one or more sources and within which water quality may be considered as being approximately uniform"--, seven supply zones were defined in the Barcelona metropolitan area, which are summarized in Table 1.

2.2 Substance selection criteria

In this study, substance selection for detection was done following four criteria: (1) polar compounds amenable by LC, (2) groups of well-known and broadly monitorized substances usually gathered under most common mixes commercially available (*e.g.* triazines, carbamates, phenylureas, phenoxy acids), (3) substances of those groups of families not present in commercial mixes but positively or probably present in the area of monitoring, (4) substances or groups of substances that have recently become relevant because they are in the list of priority substances in the field of European water policy (*e.g.* cybutrine, clorfenvinphos or pentachlorophenol) or in the Watch List of substances for European Union-wide monitoring (*e.g.* methiocarb, neonicotinoids). In addition, substances rarely monitored in Europe but recently detected at significant levels in extensive monitoring programs (Moschet et al., 2014; Schreiner et al., 2016; Stone et al., 2014) were also included (*e.g.* DEET, fluroxypyr, triclopyr), as well as some selected transformation products (*e.g.* metolachlor-ESA, desethylatrazine, desisopropylatrazine, terbuthylazine-desethyl). The selected compounds are listed in Table S1. Chemicals are described in the supporting information (SI).

2.3 Analytical Methodology

Analysis were performed in an Advance^{TM} UHPLC^{OLE} with an integrated on-line extraction option coupled to a triple quadrupole EVOQ Elite mass spectrometer, all from Bruker Daltonics Inc. On-line analyte enrichment was done on a trap column C18 (30mm x 2.1mm i.d. particle size 10 µm) and chromatographic separation was done on a C18 column (100mm x 2.1mm i.d. particle size 2 µm). Preconcentration of samples was performed by loading 10 times 75 µL of the samples through the trap column at 1 mL/min using water with 0.1% formic acid after an appropriate equilibrium flow and time (1 ml/min, 1 min). The chromatographic separation was done at 0.4 mL/min flow at 40 ºC. Solvent B was water with 0.1% formic acid and solvent A was acetonitrile acidified with 0.1% formic acid. The elution flow was initiated with 70% of B for 0.5 min, followed by a 6 min linear gradient up to 2% of B for 3 min and initial conditions re-established in 1 min and equilibrated for 2.5 min prior to the next analysis. The total chromatographic run time for one sample, including on-line SPE and LC-MS/MS was 15 min. Ionization of the sample was done with a heated ESI source (HESI) and mass resolution was set at 1 and 1.5 amu for positive ionization mode at Q1 and Q3 respectively and 2 amu for negative ionization mode both in Q1 and Q3. Acquisition was performed in a selected reaction monitoring (SRM) mode. Compound dependent parameters and collision energies voltage values were optimized for each compound by direct infusion of individual standard solutions. SRM transitions were time scheduled with an interval of 0.5 min around the expected retention time (T_r), except for some wide peaks for which it was set at 1-1.5 min. Optimized scan time for each transition was set automatically by MS Workstation software from Bruker in the range 15-50 ms for all peaks in order to obtain at least 12 points for each chromatographic peak. Two SRM transitions were selected for each compound, in order to achieve at least 4 identification points according to European guidelines for each peak (EU 2002/657/CE). For surrogate compounds, only one transition was optimized. Supporting information (Table S3) contains detailed information of the optimized parameters of this method.

2.4 Validation methodology

Validation data was evaluated in several types of natural water (upper stretch of Llobregat River, natural groundwater and drinking bottled groundwater) as well as main sources of treated water in Barcelona metropolitan area (tap water from DWTP1, DWTP2, DWTP3 and a 1:1 mixture of treated water from DWTP1 and DWTP2).

All parameters were acquired over the whole population of data obtained at intra-day and inter-day replicates in all matrices (river, groundwater and tap water from several sources) analysed in order to obtain a robust multiparametric method.

Limits of detection (LODs) were calculated by the analysis of standard solutions with decreasing concenrations (0.1-5 ng/L) for each compound and giving peaks where the relationship signal-to-noise was 3.

Accuracy and precision were calculated at low (5, 15 and 25 ng/L), medium and high (75 and 150 ng/L respectively) concentrations levels by spiking these matrix samples with mixtures of standard compounds. 15 inter-day experiments with 3 intra-day experiments for each concentration level and type of matrix were done.

Linearity between the signal of the quantification SRM transition and the concentration was evaluated for each 3 inter-day experiments, by the calculation of a ten-point linear plot over the range of 5–150 ng/L, based on a linear regression where the coefficient of determination ‘r2’ should be >0.995 and the residuals less than 15%.

Limits of quantification (LOQs) for each compound were set from validation data for the minimum concentration levels tested which fulfilled the objectives of accuracy and precision (both ≤25%). Uncertainties (u) associated with the concentrations of pesticides in water were evaluated using validation data as quadratic sums of accuracy and precision values to obtain u^2 (ISO, 1994; ISO, 2012). Expanded uncertainty (U) was obtained by multiplying the standard uncertainty by a coverage factor (k=2). Signal suppression was evaluated in all matrices as described elsewhere (Boleda et al., 2013).

2.5 Sampling and sample preparation

Samples were collected by a trained team during years 2016-2017 following an accredited procedure based on ISO 5667-5:2006. Ascorbic acid was added into drinking water samples (at 0.3 mM of sample) in order to avoid the degradation of pesticides before analysis. Sample preservation was accomplished by storing the bottles in the dark at 4 ºC. Sampling points along the Llobregat River basin were collected at points described in Figure 1, which are characteristic for their major pollution inputs in the Llobregat River.

Sampling point LLO-3 is only representative when storm episodes occur and the diverted system of Anoia River does not work properly (Quintana et al., 2016).

Groundwater was sampled directly from the wells. In some areas with contiguous wells with similar water qualities, samples are labelled like the sampling point. In the case of DWTPs 1, 4 and 5, groundwater is also collected at the intake of the facility as it results from the mixture of waters coming several wells, depending on the operational status of DWTPs at each moment. The obtained data was levelled with the same code as the equivalent groundwater sampling point.

Distributed water was sampled indistinctly from reservoirs over the territory and from sampling points distributed along the net for each defined supply zone (Table 1), as established by the EU Directive (UE) 2015/1787. The data obtained from each supply zone was integrated for a whole data analysis of each zone.

Final water from DWTPs was collected either at the exit of the facility or at its main reservoir. In the case of DWTP1 and DWTP4, samples were also collected at the end of each treatment step taking into account the hydraulic retention times.

Prior to instrumental analysis, in order to avoid suspended particles stoppleing the column in the chromatographic analysis, samples were transferred to 2 mL Eppendorf tubes and centrifuged at 8,000 r.p.m. during 20 min. 2 mL Eppendorf tubes PCR clean quality (Hamburg, Germany), and Consul 21 centrifuge from OrtoAlresa (Aljavir, Spain) were used. An aliquot of 1.5 mL of supernatant was placed in a 2 mL amber glass vial and 50 µL of 1.5 ng/mL solution of surrogates was added at each vial in order to ensure the correct performance of the overall analytical process.

Calibration (n=10) was performed by spiking a mixture of standard compounds in the range of 5-150 ng/L in ultrapure water. In those areas where quantification was expected to be less than 1/3 of LOQs, blank controls were evaluated by spiking a solution of surrogates in ultrapure water. The reliability of the method was evaluated in each set of analysis by spiking ultrapure water at 15 ng/L using several independent mixtures of selected compounds where the accuracy should be around 25%.

3. Results and Discussion

3.1 Performance of the method

Method development. Details about method development and optimization are given in the supplementary information (Table S3).

Method validation. As the method was conceived for routine control for natural and produced water intended for human consumption, the method validation plan was designed to obtain the official accreditation according to ISO/IEC 17025, which specifies the general requirements for the competence to carry out tests and calibrations.

Quality of the method parameters such as linearity, LODs, LOQs, accuracy, precision and uncertainty were calculated.

Linearity was examined over the range of 5–150 ng/L. For the ten-point calibration curves, only the selected SRM transitions for quantification were employed. Calibration curves were linear in the studied range with values of coefficients of determination of $r^2 > 0.99$ for 66 out of the 96 analysed compounds (Table S4).

LODs were calculated based on the signal-to-noise approach. Determination of the signal-to-noise ratio was performed by comparing measured signals from samples with known low concentrations of analyte with those of blank samples, and establishing the minimum concentration where the analyte can be reliably detected. A signal-to-noise ratio of 3 was used to estimate the LODs of the method. LOQs were established well above the LODs since to evaluate the robustness of the method under an accreditation frame is not mandatory to obtain the lowest LOQs. Under the European Directive (UE) 2015/1787 the LOD of the method for a compound must be lower than 25% of the parametric value (100 ng/L for pesticides). Consequently, LOQ is admitted to be three times the LOD (less than 75 ng/L). According to this Directive, more important than the presence/absence of a compound in the environment is to determinate whether its presence is relevant or not. When possible, 5 ng/L was set at a minimum LOQ because this concentration was enough to achieve both objectives (Table S4).

The optimized method allowed 45% of the compounds to have their LODs at sub-ng/L and only 6% were over 10 ng/L. Regarding validation results, for the 56% of the compounds proposed in this method (96), LOQ was set at 5 ng/L, 10% was set at 15 ng/L and for 5 compounds it was set at 25 ng/L. 27 compounds did not meet the objectives of the accreditation (Table S4).

Matrix effect (signal suppression and signal enhancement) was demonstrated to be less dependent (less than 20%) from matrix (Table S5) for most of compounds, but correction was still applied to some compounds for certain matrices in order to balance this effect. Due to the difficulty to manage matrix effects in routine analysis, matrix effects was not applied and its contributions were incorporated to the accuracy and the precision data of each compound and, consequently, at its expanded uncertainty.

Among the myriad of papers reporting the presence of emerging pollutants in the aquatic environment, only a few deal with an estimation of the uncertainty of the analytical procedure, which gives a clear evidence of the robustness and quality of the proposed methodology. Papers related to pesticide analysis (Banerjee et al., 2007; Kmellar et al., 2008; Planas et al., 2006; Quintana et al., 2001), nonylphenol (Díaz et al., 2002), dioxins (Martínez et al., 2009) or pharmaceuticals (Boleda et al., 2013; Gaudiano et al., 2008) are some of the examples found in the literature. However, the estimation of the uncertainty of analytical results is mandatory for laboratories accredited under EN45001 requirements (CEN/CENELEC, 1989). The two main approaches to calculate uncertainty are the 'bottom-up' and 'top-down' methods (Eurachem, 2012). We have employed the 'top-down' approach, which uses the validation data to estimate the uncertainty of the method from accuracy and precision (where u^2 is the quadratic sum of accuracy and precision). For most purposes, in analytical chemistry, an expanded uncertainty (U) should be used. The expanded uncertainty provides an interval within the value of the measure and it is believed to be of a higher level of confidence. U is obtained by multiplying the standard uncertainty (u) by a coverage factor (k=2). The selection of this factor is based on the desired level of confidence. Expanded uncertainty was calculated only for those compounds that reached the validation objectives. In agreement with (UE) 2015/1787 the declared uncertainty of the method should be given at parametric values of compounds (100 ng/L for pesticides). Because parametric values were not included in the validation levels, the declared uncertainty was calculated as the maximum uncertainty obtained for both upper validation levels (75 and 125 ng/L), rounded up to 5 units. For most compounds (45%) validation levels were less than 40% and none of them was over 60%, in agreement with the European Directive. For those compounds that did not reach the objectives of the validation/accreditation (27) a generic LOQ was set at 25 ng/L. Table S4 compiles the quality parameters of the method.

In summary, 72% of the 96 compounds proposed reached the validation objectives and, consequently, were able to be accredited under EN ISO/IEC 17025.

3.2 Monitoring results and discussion

3.2.1 Background.

Historical data of pesticide occurrence in Llobregat River basin shows that only a few substances have been intensively monitored (Table 2 and Table S2) in the last decades.

A review of available historical data (Tables 2 and S2) shows the predominance of triazines (atrazine, simazine, terbuthylazine, terbutryn, cyanazine) and their metabolites (*e.g.* desethyl- and desisopropilatrazine) as the main pesticide pollutants analysed in the Llobregat river basin, mostly in the lower stretch. Some other relevant pollutants that have been monitored are phenoxyacids (2,4-D and MCPA), phenylureas (diuron and isoproturon) and organophosphorus compounds (diazinon and dimethoate). Although the analytes selected in these studies were relevant, they were not sufficient in order to accurately assess the risk assessment, as previouslysuggested by some authors (Köck-Schulmeyer et al., 2012). The impact of the highly the polluted Anoia River and Rubí Streams to the LLobregat River at its low stretch should be minimized by by-pass systems. These protected systems had not been working properly in the past due to some heavy rain episodes (storm water) and to insufficient maintenance causing a severe drop of water quality in the low stretch of the river (Quintana et al., 2016).

To the best of our knowledge, there are a few reports (Köck-Schulmeyer et al., 2014; Postigo et al., 2010; Rodriguez-Mozaz et al., 2004) about the presence of pesticides in the Ter River basin apart from those related to aquifer contamination after DWTP2 catchment mouth.

3.2.2 Surface water of Llobregat River basin.

Table summarizes an overview of the results of pesticides detected during two years of monitoring (including a range of concentrations, and the maximum and median levels of two most abundant pesticides in each sampling point). Detailed results of this monitoring are available in the supporting information (Tables S6 to S9).

Results obtained for 118 samples of surface waters in 2016 and 2017 (including minimum, maximum, median, average, frequency, number of positive cases and cases >100 ng/L) are given in Table S6. A total of 21 out of the 96 compounds monitored were detected at concentrations over LOQ. Ricart *et al.* (Ricart et al., 2010) or Proia *et al.* (Proia et al., 2013) reported, in 2005-2006 and 2009 respectively, monitoring campaigns of 15-20 pesticides (triazines, phenylureas, phenoxyacids, anilides, chloroacetanilides, thiocarbamates and organophosphates) which were detected in the lower part of the Llobregat River at similar levels to those previously reported, describing generally similar concentration levels (<100 ng/L). On the contrary, other authors have reported a significant presence of pesticides in this area. Kuster *et al.* and Köck-Schulmeyer *et al.* reported unusual concentrations of phenoxyacid compounds (MCPA and 2,4-D) with more than 90% of positive samples in the range of 100-1200 ng/L (Kuster et al., 2008) and diuron and diazinon as the most ubiquitous and abundant compounds (with levels up to 818 and 132 ng/L) in the final stretch of the river (Köck-Schulmeyer et al., 2012). More recently, Masiá *et al.* (Masiá et al., 2015) detected in monitoring campaigns done in 2010-2011 a broad type of compounds as organophosphorus (chlorfenvinphos, chlorpyrifos, diazinon, dimethoate), triazines (atrazine, simazine, terbutryn), ureas (diuron, isoproturon), and others (imazalil, metolachlor, imidacloprid), being chlorpyrifos the most frequent pesticide, probably because its generalized urban and agricultural uses, applied to over all types of crops and even as soil powder for insect control. Chlorpyrifos is especially used as a substitute of other organophosphate pesticides (such as azinphosmethyl, azinphos-ethyl, chlorfenvinphos, diazinon, ethion, fenitrothion, fenthion, omethoate, and parathion-methyl and parathion-ethyl) banned by the EU (Regulation EC No 2009/1107) (Terrado et al., 2009).

As shown in the above-mentioned tables, a few pesticides could be detected in the upper stretch of Llobregat, Cardener and Anoia rivers at non-relevant concentrations. This coincides with the characteristics of these areas, since they share a low density of population and a non-intensive fodder and cereal agriculture as main activities.

Sampling point LLO-1, located in the medium stretch of Llobregat River after approximately 90 Km of the river flow and before its confluence with Cardener River, shows the presence of 10 pesticides (Table 3). Carbendanzim was the most relevant compound (with a maximum concentration of 1054 ng/L, 43% positive samples) and chlorotoluron (max. 228 ng/L and 50% frequency) the next one with a high concentration found. These are the two sole compounds with concentration levels higher than 100 ng/L. Propiconazole, a triazole fungicide acting as a cellular growth inhibitor, is also detected in several samples at a maximum concentration of 83 ng/L. All these compounds are widely spread in all Llobregat River basin and they will be present in most of the surface water sampling points. Masiá *et al.* (Masiá et al., 2015) reported the broad use of several families of pesticides in this area, specially malathion (organophosphorus) which was detected at 320 ng/L in 2010, although it as not detected in 2011. Carbenzamin, a broad-spectrum benzimidazole fungicide is widely used to control plant diseases in cereals and fruits (García-Galán et al., 2010). Merel *et al.* (Merel et al., 2018) showed that the presence of carbendazim in the Rhin River area correlates poorly with that of other fungicides used as active ingredients in plant protection products, whilst it correlates linearly with that of pharmaceuticals, suggesting that the occurrence of carbendazim in surface water mainly comes from the discharge of treated domestic wastewater, as confirmed by its detection in wastewaters.

In the Cardener River (sampling points CA-1 and CA-2) 12 pesticides were detected at low concentrations (most of medians <LOQ) with a major presence of these compounds in the final stretch (CA-2), but almost with unique detections, probably showing a scheduled pesticide application in the farming activity. However, the presence of the insect repellent DEET showed the influence of the urban WWTPs effluents. DEET is used as personal care product, or imidacloprid, a neonicotinoid insecticide of broad usage in agriculture, arboriculture, home protection, domestic animals, turf and gardening, and it is also associated with household usages. The most commonly detected compounds in the Cardener River were prosulfocarb in the upper stretch (in 6 of 13 samples taken at CA-1) and imidacloprid in the lower stretch of the river (in 6 of 13 samples taken at CA-2), being carbendanzim the compound at the highest concentration (94 ng/L). A sole study was published previously concerning the Cardener River (Masiá et al., 2015), reporting very low concentrations of a broad of

benzimidazole, phenylurea, neonicotinoid and organophosphorus families at the last stretch of the river, but making emphasis on the influence of effluents of Manresa's WWTP.

At the intake of DWTP3 (LLO-2), more than 25 km downstream of the confluence of the Cardener River with the Llobregat River, the presence of pesticides and their concentrations are still not relevant except for carbendanzim (maximum concentration 269 ng/L and 71% frequency), diazinon and metazachlor (maximum concentrations of 71 and 46 ng/L, respectively). Again, the presence of some cities located upstream, and several WWTPs with poor efficiencies for removing some pollutants could explain the presence of some of these compounds, such as DEET or imidacloprid (frequencies of 17 and 29% respectively), although their levels were low (maximum 16 ng/L). Terbuthylazine, a compound described with a chronic presence in the past at the intake of DWTP3 (Paune et al., 1998), was not present at LLO-2 in any sample, neither it was atrazine, which was detected at ≈4 mg/L in several herbicide spills in the same geographical area in the middle of the '80s (Rivera et al., 1986; Rivera et al., 1985). In 2000, simazine, atrazine and its metabolite desisopropyl-atrazine were described as relatively frequent compounds in raw water entering DWTP3 (Quintana et al., 2001). Atrazine was banned in Europe in 2004 and this could explain its reduction or absence in further campaigns. Neither terbuthylazine nor atrazine were detected, but none of the triazine metabolites related to both herbicides were detected in this study at that sampling point either. Masiá *et al.* described the absence of terbuthylazine and the presence of its transformation products probably by the photodegradation mechanism (Masiá et al., 2015). Propiconazole is also present at this sample point with a maximum concentration of 82 ng/L, but with a low frequency and median concentration (<LOQ).

Anoia River, a tributary of Llobregat River, is diverted (90%) due to its elevated pollution before its natural confluence with Llobregat river, to minimize its impact on the catchment area of DWTP1. In its upper stretch (AN-1), herbicides 2,4-D (max. 855 ng/L, 75% frequency) and prosulfocarb (max. 104 ng/L, 86% frequency) used as pre-emerging herbicide in cereal farming, were the unique common pollutants in the three upper basins identified: imidacloprid, a relatively frequent neonicotinoid, and the fungicide tebuconazole, which also protects cereal farming.

Sample points AN-2 and AN-3 (sampling point before river being diverted) reveal a severe input of the pesticide contamination, since most of the detected compounds in this study were present at these sampling points. AN-2 is located close to an intense farming vineyard area and downstream of a WWTP, which collects sewage waters of several industrial areas mainly focused on tanning industry, which uses pesticides as a preventive conservation of leather. Carbendanzim was present in all samples in this area at median and maximum concentrations of 2623 ng/L and 9574 ng/L for AN-2 and 1990 ng/L and 16866 ng/L in AN-3, respectively. This compound was not detected by Masiá *et al.* (Masiá et al., 2015) neither in AN-2 nor AN-3 in 2010. However, in 2011 it was detected at a very low concentration at AN-2, but approximately at 700 ng/L in AN-3, suggesting that the incorporation of carbendanzim in the surface water takes place between sampling points AN-2 and AN-3. Also 2,4-D, DEET, diazinon, dimethoate, diuron, imidacloprid, propiconazole, prosulfocarb and terbutryn were present at higher concentrations than 100 ng/L, at least in one sample. In addition, a concentration above 100 ng/L was also exceeded by bentazone, DEET, imidacloprid, isoproturon, propiconazole, propoxur, prosulfocarb and simazine at sampling point AN-3. As stated by Masiá *et al.* and Ginebreda *et al.* in the past (Ginebreda et al., 2014; Masiá et al., 2015), the pool of pollutants remained similar from sampling points AN-2 to AN-3, but in lesser amounts in AN-3, suggesting the importance of the environmental impact assessment of effluent of Igualada's WWTP and the later dilution due to an increse flow.

Rubí stream (RU-1), which collects industrial and urban effluents of Terrassa's and Rubí's WWTPs, is usually diverted, but it overflows during strong storms. RU-1 showed a broad presence of compounds, eight of them exceeding 100 ng/L at least in one sample (carbendazim, DEET, diazinon, diuron, imidacloprid, isproturon, MCPA and propiconazole). The phenylurea diuron and the triazole fungicide propiconazole are the main pollutants with maximum concentrations of 2127 ng/L and 2216 ng/L respectively, medians of 805 ng/L and 274 ng/L, respectively, and 100% frequencies. Concerning pesticide pollution, a few evidences existed in the past (Köck-Schulmeyer et al., 2012; Kuster et al., 2008) of its heavy pollution and only Köck-Schulmeyer *et al.* reported an average concentration of 461 ng/L of diuron as the main relevant pollutant.

Sampling point LLO-3 is located after the by-pass systems of Anoia River and Rubí stream. This sampling point is especially relevant when the by-pass systems do not work properly (*e.g.* overflow, storm water …), but this fact occurred only once during sampling campaigns with non-relevant results. In usual conditions, its environmental quality should to be comparable to LLO-2.

In 2016 and 2017, at the intake of DWTP1 (sampling point LLO-4), the profile of pesticides showed the contribution of AN-3 and RU-1, although concentrations were lower due to their dilution into the Llobregat River. The by-pass systems of Anoia River (usually the 90% of Anoia's River flow) and Rubí stream normally work well, and do not show the pesticide profile of LLO-4. Even so, these polluted waters are used to irrigate the left bank of the farming area sited in the final stretch of the river. In addition, the right bank is irrigated with downstream waters from the by-pass system, which has better water quality (in normal conditions equivalent to LLO-2 or LLO-3 quality), despite an important contribution of Abrera's WWTPs effluents, as stated Kuster *et al.* who reported 1286 ng/L of MCPA (Kuster et al., 2008). The run-off of these farming activities, added to the irrigation water usage and the chemicals applications could partially explain the profile at LLO-4. In southern countries of Europe, farms are small compared with those in northern Europe. This probably explains the variety of pesticides and application methods that need to be taken into account, because each farmer will take his own decision in terms of which pesticides to use and when to use them (Ramos et al., 2000). Industrial and urban activities in this area should not to be considered in this final stretch, since WWTPs effluents do not discharge above LLO-4 as it was verified by Köck-Schulmeyer *et al.* (Köck-Schulmeyer et al., 2011). On the other hand, in some rainy periods groundwater piezometric levels can be higher than the river level. This leads to a direct flow transfer from groundwater to surface river; although during the drought period that took place in 2016-2017 this effect did not seem to be a key factor.

Quintana *et al.* (Quintana et al., 2001) published the first data on the intake of DWTP1 (sampling point LLO-4) by a systematic sampling campaign during the year 2000. The main pesticides reported at this point were some triazines and their transformation products (max. concentrations in the 60-85 ng/l range), as well as dimethoate (max. concentration 154 ng/L). Rodriguez-Mozaz *et al.* (Rodriguez-Mozaz et al., 2004) reported high levels of some phenylureas (239 ng/L of diuron and 503 ng/L of isoproturon) which persisted in the presence of triazine compounds, but at higher levels (463 ng/L of atrazine and 2218 ng/L of simazine). Kuster *et al.* (Kuster et al., 2008) introduced the surveillance of phenoxyacids reporting high amounts of 2,4-D and MCPA (max. concentrations of 69 ng/L and 122 ng/L respectively). Since then, and over the last 15 years, other studies covering a broad group of compounds (Damásio et al., 2011; Ginebreda et al., 2014; Kampioti et al., 2005; Köck-Schulmeyer et al., 2012; Köck-Schulmeyer et al., 2011; Proia et al., 2013) reported similar occurrence and levels, including phenoxyacids, triazines (max. concentrations of simazine and terbuthylazine of 38 ng/L and 83 ng/L respectively), organophosphorus compounds (max. concentrations of diazinon and dimethoate of 132 ng/L and 42 ng/L respectively) and phenylurea compounds (max. concentrations of diuron of 54 ng/L) (Table S2).

At LLO-4, a total of 55 and 14 samples were analysed in 2016 and 2017, respectively; were carbendanzim, was present at 96% of the samples at median and maximum concentration of 92 ng/L and 1425 ng/L, respectively, thus becoming the most relevant compound. In 2016, carbendazim exceeded 26 times the concentration level of 100 ng/L (6 times in 2017). Metazachlor, propiconazole, DEET, diuron, methomyl and simazine exceeded 100 ng/L at least in one sample. Also, 2,4-D, imidacloprid, MCPA, MCPP, prosulfocarb, and terbutryn were the other most relevant compounds, but at median values <15 ng/L. At the same time, simazine and terbuthylazine, which had historically been two of the most reported pesticide pollutants at this sampling point, remained present, but at non-relevant concentrations (both medians < LOQ).

As for the policy compliance, atrazine, clorfenvinphos, chlorpyriphos, diuron, isoproturon, simazine, cybutryne and terbutryn are the amenable pesticides by this method included in the European Directive on Environmental Quality Standards (Directive 2008/105/EC). According to the watch list of substances in the three most significant sampling points, Anoia River and intakes of DWTPs 1 and 3 (AN-2, LLO-2 and LLO-4), only diuron and terbutryn showed warning concentrations. Both compounds were present at almost all samples of AN-2 and LLO-4, but the WFD's annual average value and the maximum allowable concentration were not overtaken by any samples. No breaches of the WFD were recorded during the 2016-2017 campaigns for the compounds in the scope of this method, although this pesticide had exceeded these limits in the past (Köck-Schulmeyer et al., 2012). Because its relevance, the intake of DWTP1 (LLO-4) hds been the most monitored sampling point of the river in the past, and in this study too. Downstream of DWTP1, waste water is canalized to ensure the water quality at the intakes of DWTP3 and DWTP1 but from this point to mouth surface water in not used any more so its quality is not subject matter of this work.

An overall look at these results shows that the upper stretches of these three rivers are the least polluted areas, with a gradual increase of pollution in the surface waters along the water course due to the cumulative effect of agricultural, industrial and human activities, as previously stated by Muñoz *et al.* for pharmaceuticals (Muñoz et al., 2009). On the other hand, Anoia River and Rubí stream have been reported as the most relevant inputs of pesticide contamination of Llobregat surface water due to the leaks of the by-pass systems of both waters (Quintana et al., 2016). Pesticide pollution beyond the confluence of Llobregat River with these two tributaries must then be the result of the dilution by the addition of flows or by industrial and farming practices in the final stretch of the Llobregat River. In addition, results showed that the presence of some pesticides that were detected in the past at a worrying levels (*e.g.* some triazines) is no longer a matter of concern. However, there are other pesticides with poor or non-existent concentrations in the past, that appear now as an emerging concern (*e.g.* diuron, DEET, carbendanzim, prosulfocarb). Historical data reveals how an accurate management of the infrastructures and environmental policy can improve the quality of surface water intended for abstraction of drinking water.

3.2.3 Groundwaters of Llobregat and Besòs rivers basins.

Results obtained for 82 groundwater samples (GW-LLO-1, GW-LLO-2 and GW-BES-1) during 2016 and 2017 are summarized in Table 3 and detailed in Table S7. In most cases, Llobregat River wells are sited not far from the bank along several kilometres upstream DWTP1.

GW-LLO-1 is an integrated sampling point of water from a few wells used as a unique source of water at DWTP4. Carbendanzim (maximum and median concentrations of 218 ng/L and 85 ng/L, respectively and 100% frequency of appearance and 6 times concentration levels >100 ng/L in 2016) and diuron (maximum 50 ng/L, median 38 ng/L and 100% of frequency in 2017) were the two most relevant identified compounds at this sampling point. Several triazines such as terbutryn, simazine, triazine metabolites (*e.g.* desisopropylatrazine with maximum 68 ng/L, median 28 ng/L and 60% of frequency of appearances), 2-hidroxyterbuthylazine and desethylterbuthylazine were present in some samples, as well as imidacloprid and propiconazole. At this sampling point, no data concerning pesticide pollution had been previously reported.

GW-LLO-2 is an integrated sampling point of several wells used at DWTP1 when quality of raw water from Llobregat river is not satisfactory or is insufficient. Most pesticides identified in GW-LLO-2 are also present in the river water at the intake of DWTP1 (LLO-4) due to their proximity. So, the natural and/or artificial recharge of the aquifer is closely related to the quality of the surface water, showing similar inorganic profiles of both surface and groundwaters (Martin-Alonso, 1994). In addition, the average levels of groundwater's piezometers and the annual flow of the Llobregat River are directly related (*e.g.* period 1970-1995, Figure S2) around DWTP1 (sampling points GW-LLO-2, LLO-4 and DWTP1) due to natural or artificial recharge of the aquifer from surface water.

Carbendanzim, diuron, propiconazole and tebuconazole exceed 100 ng/L at least in one sample with maximum values of 426 ng/L, 333 ng/L, 100 ng/L and 110 ng/L, respectively. Among the triazines, only terbutryn (max. 37 ng/L), terbuthylazine and its metabolite desethylterbuthylazine were present at levels close to their limit of quantification. In the past, Quintana *et al.* (Quintana et al., 2001) reported for first time concentrations of triazines (max. concentration of simazine 73 ng/L and terbuthylazine 53 ng/L) and triazine metabolites slightly over their LOQs, results that were confirmed a few years later by Rodriguez-Mozaz *et al.* (Rodriguez-Mozaz et al., 2004) (max. concentration of simazine 153 ng/L) and Kampioti *et al.* (Kampioti et al.,

2005) (max. concentration of simazine 54 ng/L and low levels of phenylureas and organophosphorus compounds).

Groundwater of Besòs River (sampling point GW-BES-1) is the only source of water at DWTP5. The sole historic data available in the literature (Quintana et al., 2001) was collected at the beginning of 2000s in the preliminary studies prior to upgrade DWTP5 from the ancient, centennial and steam engine powered DWTP. The presence of triazines (atrazine, simazine, terbuthylazine and atrazine metabolites) was reported but the list of analysed compounds was limited. In this study, only 7 samples were analysed in 2016 and 2017. However, 17 pesticides and metabolites were detected in almost all samples. Carbendanzim and chlortoluron with median values of 101 ng/L and 131 ng/L, respectively, exceeded 100 ng/L in all samples of 2016. Triazines (atrazine, metribuzin, simazine, terbuthylazine and metabolites and terbutryn), other phenylureas (diuron, fenuron, isoproturon) and some miscellaneous groups (bentazone, metolachlor and metabolite, imidacloprid, tebuconazole) were present in the range of 20-50 ng/L, but the sum of all pesticides for each sample also exceeded the WFD recommendations.

3.2.4 Drinking water of Barcelona's metropolitan area.

Results obtained for 482 samples of drinking water analysed in 2016 and 2017 (minimum, maximum, median, average, frequency and >100 ng/L cases) are summarized in Table S8. The three main sources of drinking water of Barcelona Metropolitan area are DWTP1, DWTP2 and DWTP3 which serve non-blended drinking water to zones A, E and C1, respectively (Figure 3).

Zone A (126 analysed samples) shows very few detections of pesticides at very low concentrations. Metazachlor and azoxystrobin were the most commonly identified compounds (frequency of 8% and 6%, respectively) with a maximum value for both compounds of 12 ng/L, and DEET and carbendazim were detected only in one sample only (32 ng/L in 2016 and 31 ng/L in 2017, respectively). Results showed an effective removal of pesticides after the treatment process on DWTP1, especially when the raw water of this facility (sampling points LLO-4 and GW-LLO-2) was severely polluted by pesticides. Previously reported studies of pesticide removal in DWTP1 were performed when the facility was still using the conventional train (ozonation and GAC filtration after the secondary treatment). Thus, Rodriguez-Mozaz *et al.* (Rodriguez-Mozaz et al., 2004) described the complete removal of 239 ng/L of diuron in the ozonation stage and the progressive elimination of 2218 ng/L of simazine from surface water to 32 ng/L in final drinking water (approximately 45% and further 95% of removal in ozonation and GAC filtration respectively), whereas Kampioti *et al.* (Kampioti et al., 2005) described the 65% and 91% removal in ozonation and GAC filtration stages, respectively, from total pesticides concentration of 516 ng/L to 47 ng/L in final drinking water. In order to properly manage the salinity of Llobregat River and reduce the undesired production of disinfection by-products imposed by WFD in 2009, DWTP1 was enlarged with a parallel stage of advanced treatment, which employs ultrafiltration (UF) and reverse osmosis (RO). In order to assess the pesticide removal efficiency in this new configuration since 2009 in DWTP1's treatment, five sampling campaigns took place between September 2016 to January 2017 period in all stages of treatment. Samples were collected at different times according to the hydraulic retention time in the facility. Results are shown on Table S9 and reveal a similar removal level for conventional treatments, as previously reported. Carbendazim, imidacloprid, metazachlor and terbutryn (frequency of appearance of 100%, 100%, 75% and 50%) were the most frequently detected at the intake of the DWTP1, being carbendanzim the compound most poorly removed in the classical process, although 10 other compounds were completely removed after ozonation stage, and 4 compounds remained below 10 ng/L after GAC filtration.

On the other hand, the advanced treatment revealed a complete removal of pesticides at the end of this stage. In this DWTP, blending ratios between both conventional and advanced treatments depend on the operational status at each moment, and it has been proved to be a smart strategy to manage the presence of pesticides and other pollutants in finished water, in accordance with the drinking water directive.

Zone E is supplied with water from the Ter River once treated at DWTP2 and, in a less extent, with water from the Besòs Aquifer, treated at DWTP5. In zone E (122 samples analysed), the presence of pesticides in water produced in DWTP2 located in the Ter River is reduced to terbuthylazine, fenuron, DEET and azoxystrobin (frequency of appearance of 13%, 5%, 2% and 1% respectively), being fenuron the most relevant compound in terms of concentration at maximum levels of 71 ng/L and median of 13 ng/L. Historical and actual data on the presence of pesticides in the Ter River at the intake of the DWTP2 and about their behaviour in the conventional treatment stages is not available in the literature. However, in the past, Quintana *et al.* (Quintana et al., 2001) reported the habitual presence of simazine, atrazine and metolachlor (from LOQs to 30-65 ng/L range) in treated water from DWTP2. The presence of metolachlor-ESA in zone E (one detection at 7 ng/L) can be explained by the regular use of metolachlor in the Ter basin, as it has been reported in the past.

Contribution of DWTP5 to supply zone E was negligible in 2016 and 2017, and it has been introduced in this study as a case study. Due to chronical pollution of Besòs River basin, its groundwater can only be used as a source of drinking water after an advanced treatment by nanofiltration (NF) and reverse osmosis. Due to the discontinous operation of DWTP5, only one sample was analysed (not shown individually and integrated to Zone E results), which showed the expected complete removal of all pesticides from raw water after a membrane-based treatment. The efficiency of treatment' stages of DWTP5 had been previously evaluated by Quintana *et al.* (Quintana et al., 2001) reporting the isolated presence of simazine, atrazine and desisopropylatrazine (from LOQs to 30-65 ng/L range) from a high polluted source of water (GW-BES-1). This could be explained by the low efficiency of advanced treatment stages (NF and RO) used in this DWTP5 compared to those used in DWTP1 (UF and RO).

In zone C1 (40 samples analysed), drinking water is supplied by DWTP3, located in the upper course of the Llobregat River. The presence of pesticides is reduced to fenuron and DEET (frequencies of appearance of 7% and 4%, respectively). Fenuron is the most relevant compound with maximum concentration levels of 63 ng/L and median of <LOQ. These results contrast with those reported for the water coming from DWTP3. Terbuthylazine was then described as a chronical pollutant in finished water (Paune et al., 1998) before the installation of the GAC filtration stage in DWTP3, whereas several years later, triazines (Quintana et al., 2001) and phenoxyacids (Kuster et al., 2008) were identified in finished water when GAC filtration was already operating. The decrease of pesticide detection in this water can be explained by the improvement of the quality of raw water at the intake of DWTP3 at that time (see sampling point LLO-2, Table S6), but also because the facility recently improved its potabilization process by the addition of an electrodialysis reversal treatment technology stage.

Drinking waters from B1, D and C2 distribution zones (see Table S8) are mainly blended waters coming from A, E and C1 supply zones and the occurrence of pesticides in B1, D and C2 should be correlated with them and their blending proportions. Therefore, they will not be discussed in detail. B1 and D serve drinking water to more than a half of a million and a million of people, respectively. During 2016-2017, zone C2 showed the absence of pesticides, while zones B1 and D showed the presence of azoxystrobin, propiconazole and terbuthylazine at very low frequencies of appearance and concentrations. Fenuron was detected in both supply zones at non-negligible concentration (max. concentrations of 69 ng/L and 76 ng/L), but at a very low frequencies of appearances.

Zone B2 is a small area (40000 inhabitants) supplied with groundwater from four wells at GW-LLO-1. Drinking water of Zone B2 is produced in DWTP4, which is composed by two little facilities with treated water from two wells each. In order to manage the chronic presence of chlorinated and non-chlorinated pollutants in this sampling point (Carrera et al., 2017; Guardiola et al., 1989; Martí and Ventura, 1997; Ventura et al., 1997), four stripping towers, prior to chlorination stage, were installed at each facility in the past. Drinking water resulting from DWTP4 showed the persistence of some pesticides (2-hydroxyterbuthylazine, desisopropylatrazine, diuron and imidacloprid) (Tables S7 and S8) at unaltered concentrations from groundwater to drinking water, probably due to the simplicity of both facilities treatment. However, carbendanzim was present in most samples of raw water at high concentrations (median of 85 ng/L in 2016 at GW-LLO-1, Table S7), although it was completely removed in drinking samples (Table S8). In order to study the removal of carbendanzim concentration in the treatment, a one-time sampling campaign was carried out (Table S10) and samples were collected at different times and stages according to the hydraulic retention time along the facility. As expected, the low volatility of carbendanzim (vapour pressure of 10^{-4} KPa) and its concentration in groundwater remained unaltered after the stripping stage, but it dropped down after the final chlorination stage, showing a fast degradation with chlorine not previously reported.

In summary, the presence of pesticides occurs at very low frequencies in a large number of analysed samples (288 and 194 during the years 2016 and 2017 respectively) in the seven distribution zones. The three main sources of Barcelona metropolitan area drinking water (DWTPs 1, 2 and 3) operate properly to manage pesticide pollution of raw water and serve to population safe drinking water, according to the Directive (UE) 2015/1787.

One of the goals of this study was to widen the knowledge of pesticide occurrence in order to manage the risk assessment of drinking water distributed to population in Barcelona and its metropolitan area, according to the ISO 22000 accreditation. According to this regulation, a good risk evaluation should be the consequence of a good risk identification and quantification to take the right preventive actions and to establish control plans of the identified critical points in the whole system. In addition, risks should be identified at each stage of the system, based on historical data and/or objective evidences, like the results of this study. As part of the accreditation process, a review of historical data of pesticide occurrence along the system (sources of water, stages of DWTP1 and distribution system) were performed. However, data collected in the past was limited to non-polar pesticides and selected medium and polar compounds. An effort to improve the knowledge of the presence of polar, medium polar, emergent pesticides and metabolites along the system was undertaken.

Risks evaluation (not shown) were performed from data analysis (Tables S6, S7 and S8) using a previous methodology (Ganzer et al., 2011a; Ganzer et al., 2011b; López-Roldán et al., 2016). This data reveals that all water produced in DWTPs 1, 4 and 5 is safe and satisfies the Directive (UE) 2015/1787; the treatments used for water production are appropriate, and any corrective action should be taken under UNE-EN 22000 compliance. The pesticide list of this method will be included in the safety control plans of the drinking water company for future monitoring of these compounds in the whole system in order to improve the management of the sanitary risk of population in drinking water consumption. Risk analysis of DWTPs 2, 3 and SWTP was not performed because they are managed by other water companies. In addition, surveillance and prevention and remediation measures of natural waters and groundwater should be a government responsibility according to the EU Water Framework Directive.

4. Conclusions

On-line extraction-UHPLC/MS/MS analytical method described herein for the determination of 96 polar and medium-polar pesticides in natural and drinking water samples was suitable for their determination at ng/L levels. Good performance in terms of linearity, accuracy, trueness, uncertainty and limits of detection and quantification have been demonstrated for most compounds under the EN ISO/IEC 17025:2005 accreditation requirements. Validation results demonstrate the robustness of the method and its suitability in laboratory routine analysis.

Two years of wide monitoring have been conducted for these compounds in surface waters and groundwaters of Llobregat River and Besòs River basins.

Results from this study show the presence of some pesticides already monitored in the past and 75 new compounds not previously surveyed.

In the Llobregat River basin and in drinking water from the Barcelona metropolitan area, 37 pesticides were found at least in one sample, of which 26 had never been detected before in these areas, indicating the relevance of new emerging pesticides in the monitored lists.

While 14 pesticides appeared widely spread at non-negligible concentrations in natural waters intended for abstraction of drinking water; 61 were not found in any sample.

Although 15 pesticides could still be detected in treated waters, their concentrations were much lower than those in the sources (below the LOQ many times), which demonstrates the efficiency of advanced treatments in the DWTPs involved in the production of tap water served in Barcelona city and its surrounding area, primarily in DWTP1 since membrane-base treatment was included in the DWTP's treatment lines. Consequently, in terms of risk assessment, results showed that no corrective measures are needed at these particular drinking water facilities regarding pesticide contamination.

Conflicts of interest

We wish to confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.

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Supply zone	Source of drinking water	Waterwork	Type of water	Inhabitants served
A	R2	DWTP1	Surface water and groundwater from Llobregat River	242130
B1	R1 + R2	DWTP1+DWTP2+DWTP3+ (SWTP)	Llobregat River + desalinated water from sea + occasionally Ter River	517300
B2	DWTP4 + groundwater	DWTP4	Groundwater from wells around DWTP4	39500
C1	R4	DWTP3	Surface water from Llobregat River before Anoia River confluence	10200
C2	R4 + groundwater	DWTP3	R4 + groundwater non-related to Llobregat River system	4350
D	R1 + R2 + R3	DWTP1+DWTP2+DWTP3+SWTP	Llobregat River + Ter River + desalinated water from Mediterranean sea	1272200
E	R3 + groundwater	DWTP2 + (DWTP5)	Ter River + occasionally groundwater of Besos River	402200

Table 1. Barcelona metropolitan area supply zones (in brackets minor sources of water)

References	Bibliographic references	Sampling period	Sampling area	Results	Methodology
A	Rivera *et al.* (1985)	2 months	Industrial wastewaters discharded directly to the river up sampling point LLO-2	Table S2	LLE-GC/MS (SIR)
B	Rivera *et al.* (1986)	one-time integrated sample (34 h)	Industrial dumping up sampling point LLO-2	Table S2	SPE-GC/MS (SIR)
C	Paune *et al.* (1998)	6 months	Raw and produced water of DWTP3	Table S2	SPE-GC/MS
D	Quintana *et al.* (2001)	2000	Produced water of DWTP1, 2 and 3, groundwater of DWTP1 and 5	Table S2	SPE-GC/MS (SIR)
E	Rodriguez-Mozaz *et al.* (2004)	6 months of 2002	Groundwater and produced water of DWTP1 in all treatment phases	Table S2	SPE-LC/MSMS
F	Kampioti *et al.* (2005)	June 2003	Groundwater and produced water of DWTP1 in all treatment phases	Table S2	On-line SPE-LC/MSMS
G	Damasio *et al.* (2008)	4 months during 2002-2004 period	Basins of Llobregat, Anoia, Cardener and Besos rivers	summarized and global data only avaible	Bioassays
H	Kuster *et al.* (2008)	1 months in 2003-2004 each	Basins of Llobregat, Anoia, and Cardener rivers	summarized data	On-line SPE-LC/MSMS
I	Terrado *et al.* (2009)	2003-2006	Basins of Llobregat, Anoia, and Cardener rivers	summarized data from database analysis	Chemometric model from external data
J	Postigo *et al.* (2010)	2007-2008	Groundwater of delta of Llobregat and Ter rivers	summarized data	On-line SPE-LC/MSMS
K	Ricart *et al.* (2010)	spring and autum 2005-2006	Basins of Llobregat and Anoia rivers	summarized data by pesticide families	On-line SPE-LC/MSMS
L	Damasio *et al.* (2011)	1 month of 2008	Middle and final strech of Llobregat river	Table S2	
M	Köck-Shulmeyer *et al.* (2011)	1 month of 2008	Final strech of Llobregat river	Table S2	On-line SPE-LC/MSMS
N	Cabeza *et al.* (2012)	2008-2010	Delta of Llobregat river.	summarized data. No equivalent sampling points with this study.	LC, MS, GC
O	Köck-Shulmeyer *et al.* (2012)	2009-2010	Basins of Llobregat, Anoia, and Cardener rivers	Table S2	On-line SPE-LC/MSMS
P	Proia *et al.* (2013)	2 months of 2009	Middle and final strech of Llobregat river	Table S2	Biofilms
Q	Ginebreda *et al.* (2014)	spring and autum 2005-2006	Basins of Llobregat and Anoia rivers	Table S2	On-line SPE-LC/MSMS
R	Köck-Shulmeyer *et al.* (2014)	2007-2010	Groundwater of deltas of Llobregat and Ter rivers.	summarized data by analytes. No equivalent sampling points with this study.	On-line SPE-LC/MSMS
S	Masiá *et al.* (2015)	4 months during 2010-2011 period	Basins of Llobregat, Anoia, and Cardener rivers	summarized data and Table S2	SPE-GC/MSMS

Table 2. Bibliographic references of historical pesticides concentration data in the river basins and drinking water related with Barcelona metropolitan area. Table S2 summarises the results when is possible with analog sampling points and a value for each analyte.

sampling point	samples analyzed (2016-2017)	Pesticides detected >LOQ (Total n=96)	range sum of pesticides/sample (ng/L) (1)	Substance with highest conc.	Max conc (ng/L)	Median (ng/L)	2nd substance with highest conc.	Max conc (ng/L)	Median (ng/L)
Surface water									
LLO-1	13	13	a.c.d. - 1050	Carbendazim	1054	<LOQ	Chlorotoluron	228	10
CA-1	13	5	a.c.d. - 60	Prosulfocarb	34	<LOQ	2,4-D	32	<LOQ
CA-2	13	11	a.c.d. - 160	Carbendazim	94	<LOQ	Imidacloprid	31	12
LLO-2	13	12	a.c.d. - 270	Carbendazim	269	36	Propiconazole	82	<LOQ
AN-1	13	6	15 - 880	2,4-D	855	26	Prosulfocarb	104	7
AN-2	13	22	150 - 10530	Carbendazim	9574	2623	Dimethoate	415	<LOQ
AN-3	13	27	200 - 3080	Carbendazim	16866	1990	Simazine	456	30
LLO-3	1	4	30 - 530	Bentazone	13	<LOQ	Dimethoate	10	<LOQ
RU-1	13	21	390 - 3580	Propiconazole	2216	274	Diuron	2127	805
LLO-4	69	27	a.c.d. - 1700	Carbendazim	1425	92	Metazachlor	995	13
Groundwater									
GW-LLO-1	23	10	41 - 350	Carbendazim	260	85	Atrazine-desisopropyl	68	28
GW-LLO-2	52	12	a.c.d. - 1010	Carbendazim	426	<LOQ	Diuron	333	8
GW-BES-1	7	17	25 - 530	Chlorotoluron	145	131	Carbendazim	126	66
Drinking water									
ZONE A	126	6	a.c.d. - 24	DEET	32	<LOQ	Carbendazim	31	<LOQ
ZONE B1	63	3	a.c.d. - 70	Fenuron	69	<LOQ	Propiconazole	21	<LOQ
ZONE B2	31	7	15 - 170	Propiconazole	67	<LOQ	Diuron	49	30
ZONE C1	40	3	a.c.d. - 60	Fenuron	63	<LOQ	DEET	27	<LOQ
ZONE C2	7	-	a.c.d.	-	-	-	-	-	

ZONE D	93	3	a.c.d. - 90	Fenuron	76	<LOQ	Azoxystrobin	8	<LOQ
ZONE E	122	4	a.c.d. - 90	Fenuron	71	<LOQ	DEET	29	<LOQ

Table 3. Overview of most detected pesticides and ranges of concentration in all sampling points during years 2016-2017.

(1) a.c.d. = any compound detected above each LOQ.
Note: For the calculation of the medians, concentrations below LOQ were defined as 1/2 LOQ.
Note: 2-hydroxyterbuthylazine, Acetamiprid, Atrazine, Cybutrine, Desethylterbuthylazine, Diazinon, Isoproturon, MCPA, MCPP, Metalaxyl, Methiocarb, Metholachlor-ESA, Methomyl, Metolachlor, Metribuzin, Propamocarb, Propoxur, Propyzamide, Tebuconazole, Terbuthylazine, Terbuthylazine-2-hydroxy, Terbuthylazine-desethyl, Terbutryn were also identified at levels >LOQ in some sampling points.

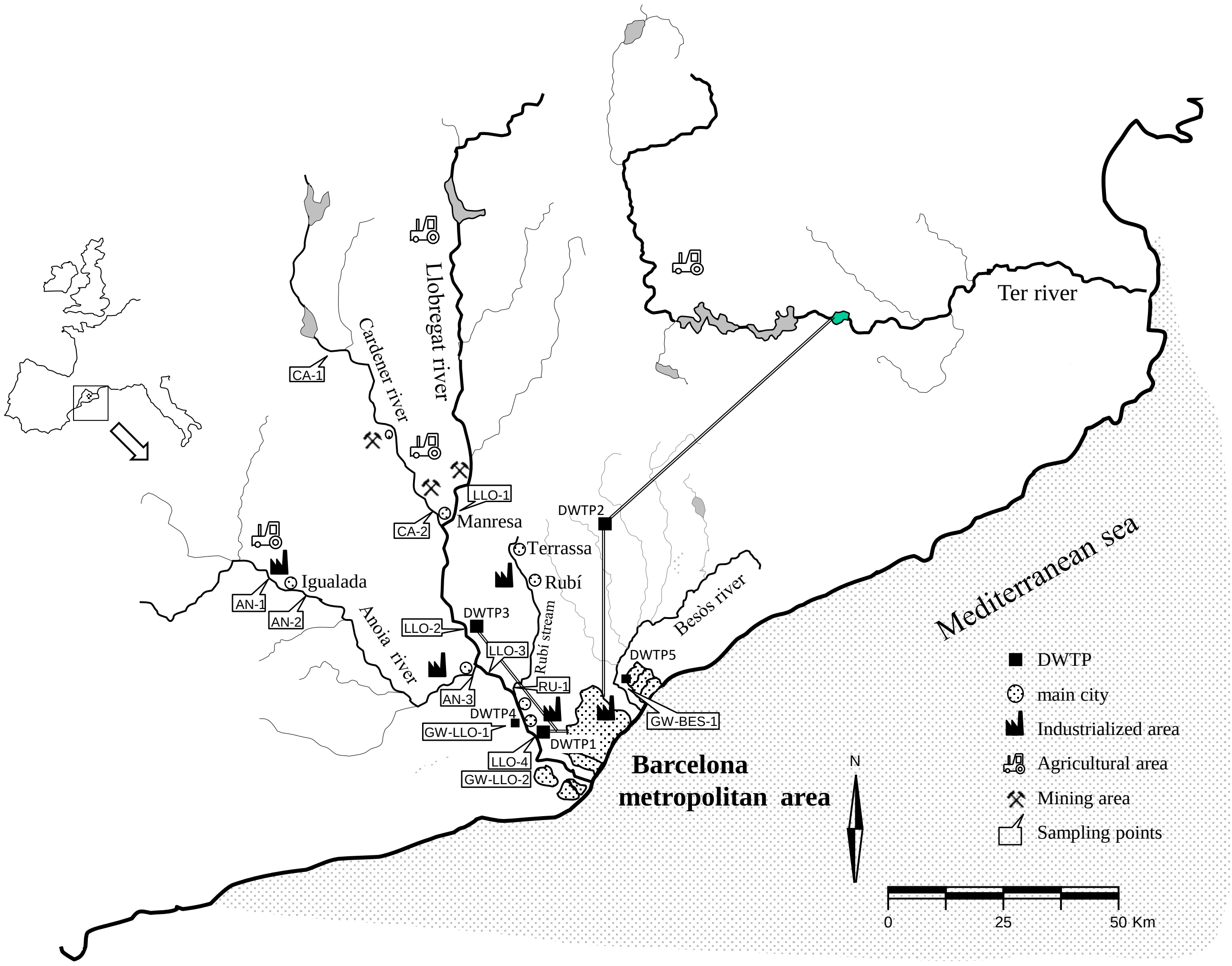

Figure 1. Site description and sampling points related to river basins and natural waters involved in Barcelona metropolitan area drinking water production.

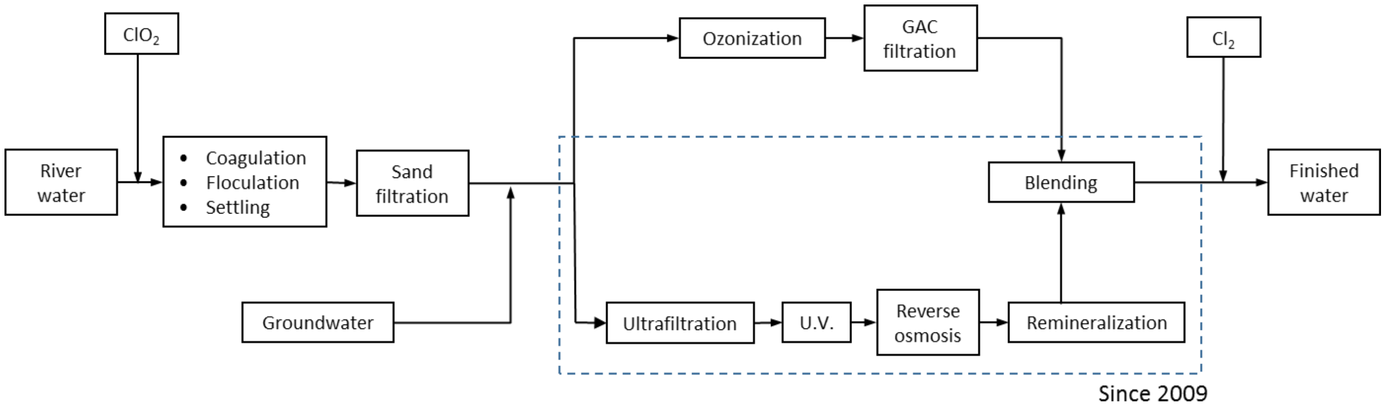

Figure 2. Diagram of DWTP1 treatment. New advanced treatment is remarked.

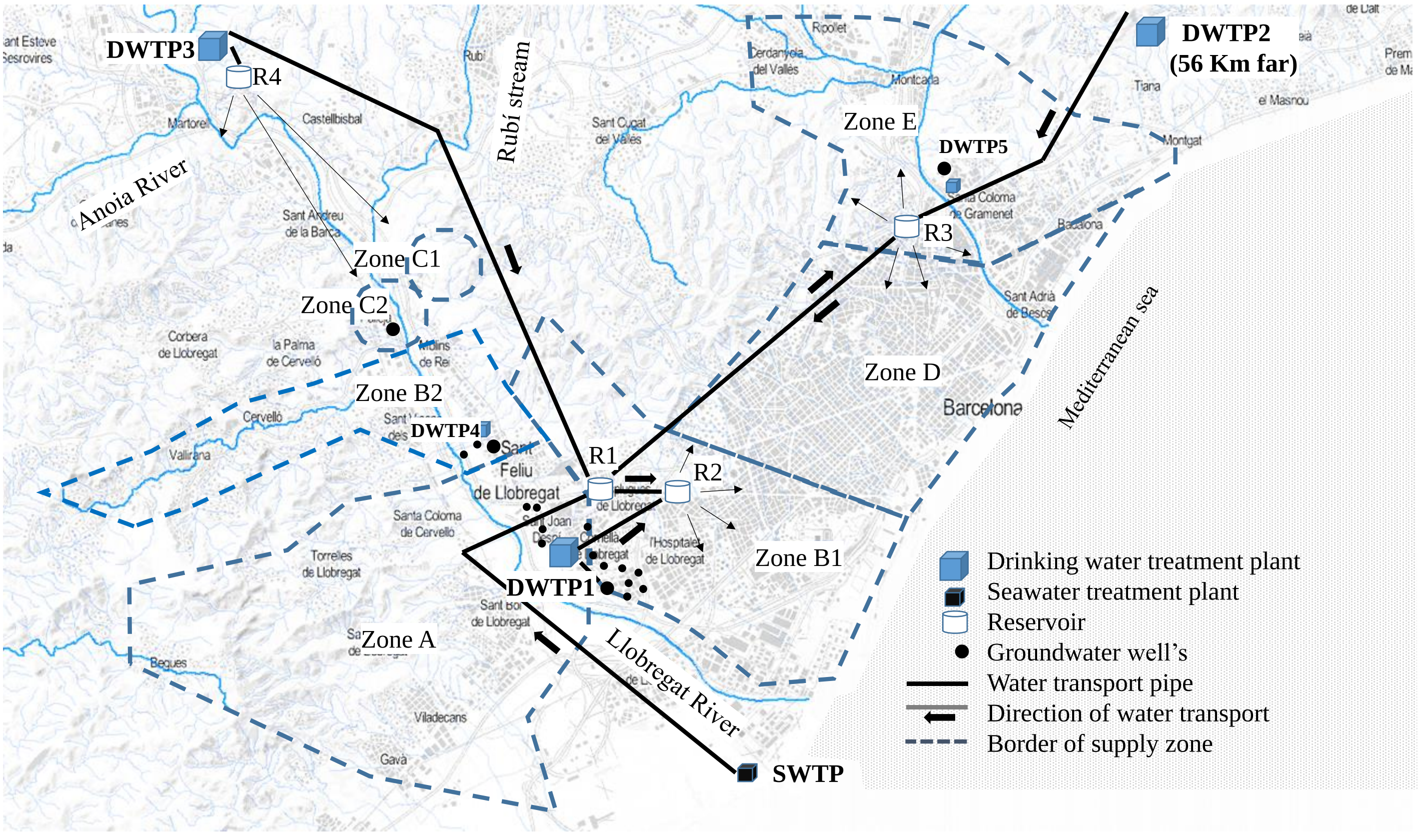

Figure 3. Barcelona metropolitan area drinking water distribution system.

Supporting Information

Occurrence of pesticides in natural and drinking waters in Barcelona City and its metropolitan area (NE Spain) by an on-line extraction and ultra-high-pressure liquid chromatography-tandem mass spectrometry multi-residue method according to ISO/IEC 17025

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minimum level) of wells associated with drinking water production at DWTP1 (sampling point GW-LLO-2) for the period of 1970 to 1995.

1. Site description

1.1 Llobregat River

Llobregat River is 160 Km long and it flows from north to south of central Catalonia to the delta sited in the Barcelona metropolitan area. Cardener and Anoia Rivers are the main tributaries. Cardener River has a low antropogenic pollution impact over Llobregat River but it goes through a saline soil which has a major impact on the organoleptic quality of drinking water in the Barcelona metropolitan area, as well as in the management of several DWTPs along the final strech of the river due to the need to reduce the water salinity. Anoia River basin is a very industrialized area where tannery industries and vineyard farming are the main spot of pesticide pollution. The Rubí Creek is another spot of industrial pollution. In 1960s-1970s, in order to improve the quality of the surface water at DWTP1 intake, especially in drought periods or industrial spills, both Anoia River and Rubí Creek, as well as some WWTPs in these areas with higher flow or polluted effluents, were diverted. However, leaks can occur due to deficient maintenance or floods, compromising the water quality at DWTP1 intake (Quintana et al., 2016). The final strech of Llobregat River is densely populated and highly industrialized, and it has a major impact to the aproximately 30 WWTPs effluents along the river length (around 137 Mm^3/year (Ginebreda et al., 2010)) and to the overall water cycle. To reduce the salt content in raw water and organic precursors of disinfection byproducts; DWTP1 and DWTP3 improved their water production using advanced treatments which also provided an improvement of both chemical and organoleptic (taste and odour) quality of water.

1.2 Ter River

Ter River is 200 Km long and it flows from north to east of Catalonia, far of the Barcelona metropolitan area, through an agricultural area. After three reservoirs systems, the 75 % of the river flow is diverted by a pipeline 56 Km long to a DWTP2 sited in Cardedeu, which serves drinking water to central Catalonia and to the Barcelona metropolitan area by another pipeline (80 km long). To the best of our knowledge, there are few reports (Köck-Schulmeyer et al., 2014; Postigo et al., 2010; Rodriguez-Mozaz et al., 2004) about pesticides' occurrence at Ter River apart from those related to aquifer contamination after DWTP2 catchment to mouth.

1.3 Groundwater

In its final stretch, the aquifer of Llobregat River is 115 Km^2 wide and contains 100 Hm^3 of groundwater which has been extensively used for water production for more than a century. At present, it contributes to the 10 % of drinking water consumption in the Barcelona metropolitan area. The wells intended for water production are sited close to DWTP1 in a very high industrialized area where chronical pollution of groundwater during last 50 years by heavy metals or chlorinated compounds (Guardiola et al., 1989) led to groundwater extraction for human consumption dropped down in the last decades in several wells. Groundwater extraction is performed in two areas, where the main one comprises around 15 wells (samplings points gathered to GW-LLO-2, Figure 1). Water is transported from these wells to DWTP1 and blended with surface water.

1.4 Drinking water treatment plants (DWTP)

DWTP1 (7 m^3/s) is sited in the last stretch of Llobregat River, before the discharge of bypass system of Anoia River, Rubí Creek and several industrial and urban wastewater effluents. After an initial removal of gravel and coarse sand, pre-disinfection with chlorine dioxide is followed by coagulation and sedimentation, and the clarified water is driven by gravity through open sand filters. The groundwater from the aquifer of the Llobregat River is then incorporated at the sand filters output. At this stage, the water production is split between a conventional refining treatment including ozonization followed by filtering through granular activated carbon (GAC), and an advanced treatment line that uses membrane technology. In the advanced process, the blended groundwater and sand filtered water flow to several chambers where the ultrafiltration (UF) membrane equipment is submerged. The output of UF is pumped to reverse osmosis (RO) racks previous disinfection with ultraviolet radiation. The produced water by this path needs to be remineralized with calcium carbonate. Both conventional and advanced treatments of produced water are blended in a chamber where a final disinfection using chlorine is performed. The percentage of water production in both treatments is variable and it depends on the raw water quality (Figure 2).

2. Chemicals

Most of triazines, urea, phenoxyacids, carbamates and organophosphorous compounds were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany) as commercial mixtures referenced as Pesticide Mix-34, Mix-95, Mix-54 and Mix-235 respectively. Compounds non-included in these reported commercial mixtures were purchased from A2S Analytical Standards (Saint Jean d'Illac, France) as custom mixtures. Compounds not included in any mixture were purchased individually from Dr. Ehrenstorfer GmbH; Sigma-Aldrich (St Louis, MO, USA); A2S Analytical Standards and AccuStandard (New Haven, CT, USA). Isotopically labeled compounds used as surrogates were purchased as custom mix from A2S Analytical Standards and individually from Dr. Ehrenstorfer GmbH and Sigma-Aldrich. A list of the target compounds including commercial details is given in Table S1 (supporting information).

Stock mixture solutions of analytes and surrogates were prepared in hypergrade LC-MS acetonitrile (ACN) at 100 ng/mL and stored in the dark at -20 ºC. Calibration solutions (5-150 ng/L) and surrogate solution (2.5 ng/mL) were preparated in ultra-pure reagent water by appropriate dilution of the above standard solutions.

Formic acid was purchased from Fluka (Büchs, Switzerland). Ultrapure water was produced using a filtering system from Elga (High Wycombe, UK). ACN was purchased from Merck (Darmstadt, Germany). Nitrogen (99.98 % pure) supplied by Nitrogen generator from Alliance (Evry, France) was used for the API source. High purity Argon obtained from Carburos Metálicos (Cornellà de Llobregat, Spain) was used as a collision-induced gas (CID gas) in the triple quadrupole instrument.

3. Analytical instrumentation

3.1 On-line SPE-UHPLC

Analysis were performed in an UHPLC with an integrated on-line extraction option coupled to a triple quadrupole mass spectrometer. The system from Bruker Daltonics Inc. (Fremon, CA, USA) consists on a paired PAL-xt.24 autosampler from CTC Analytics AG (Zwingen, Switzerland), two six port valves, two LC pumps and a additional third pump for on-line analyte enrichment on a trap column Intensity Solo HPLC Trap Column C18 10 2x30 from Bruker (30mm x 2.1mm i.d. particle size 10 µm), an analytical column Intensity Solo HPLC Column, C18 2 2x100 (100mm x 2.1mm i.d. particle size 2 µm), a liquid chromatograph Advance^{TM} UHPLC^{OLE} coupled to a triple quadrupole EVOQ Elite mass spectrometer with an heated ESI source (HESI). Preconcentration of the samples was performed by loading 10 times 75 µL of the samples through the trap column at 1 mL/min using water acidified with 0.1 % formic acid (solvent C) as a mobile phase after an appropriate equilibrium flow and time (1 ml/min, 1 min). When 0.75 mL of the sample is loaded in the trap column, a multiport valve is switched to connect the trap column with the analytical column. The chromatographic separation was done at 0.4 mL/min flow at 40 ºC. Solvent B was water acidified with 0.1 % formic acid and solvent A was ACN acidified with 0.1 % formic acid.

The gradient was initiated with 70 % of B for 0.5 min, followed by a 6 min linear gradient up to 2 % of B for 3 min and initial conditions re-established in 1 min and equilibrated for 2.5 min prior to the next analysis. The total chromatographic run time for one sample including on-line SPE and LC-MS/MS was of 15 min.

3.2 HESI-(QqQ) MS/MS analyses

Heated electrospray ionization source (HESI) parameters were fixed as it follows: spray voltage 4.5 kV and 4 kV for positive and negative ionization mode respectively, cone voltage set at 50 V, heated probe temperature and flow at 400 ºC and 20 internal units of flow, cone temperature and flow at 350 ºC and 20 units, nebulizer gas flow at 50 units, exhaust gas on, using N_2 in all HESI flows and using Argon at 1.5 mTorr pressure as a collision gas on Q2. Mass resolution was set at 1 and 1.5 amu for positive ionization mode at Q1 and Q3 respectively and 2 amu for negative ionization mode both in Q1 and Q3.

Acquisition was performed in selected reaction monitoring (SRM) mode, and compound dependent parameters and collision energies voltage values were optimized for each compound by direct infusion at 0.8 mL/h of 1 ng/ µL of individual standard solutions.

3.3 Optimized SRM transitions

SRM transitions were time scheduled with an interval of 0.5 min around the expected retention time (T_r) except for some wide peaks which was set at 1-1.5 min. Optimized scan time for each transition were set automatically by MS Workstation software (V. 8.2.1) from Bruker in the range 15-50 ms for all peaks in order to obtain at least 12 points for each chromatographic peak. Two SRM transitions were selected for each compound, in order to achieve at least 4 identification points according European guidelines for each peak (EU 2002/657/CE). For surrogate compounds only one transition was optimized.

4. Method optimization

SRM transitions were optimized by infusion of individual substances. Each transition was chosen in order to obtain both better intensity and selectivity of the transition. Even though 2002/657/EC European Union Decision(EU, 2002) is not mandatory for water analysis, it was chosen as a guideline for criteria regarding to mass spectrometric detection. In this way, two SRM transitions were selected for each compound and a single transition for labelled compounds. Most of transitions are two daughters ions from an unique precursor ion (4 identification points) but when an isotopic cluster exist involving the parent ion it was used to increase the specifity of the identification (5 identification points). The maximum allowed tolerances for relative ion intensities using LC-MS/MS, expressed as a percentage of the intensity of the most intense transition were considered for a positive identification. HESI parameters were unique for all method and were optimized taking account the overall response. Table S3 summarizes the LC-MS/MS optimized compound dependent parameters used for each pesticide which includes labelled compounds used as surrogates.

Regarding chromatographic separation, the use of acidified ACN instead of MeOH proved to be the most suitable for most compounds obtaining a better chromatographic resolution and narrower peaks. Several linear gradients were tested in order to obtain the best separation using standard HESI parameters. Afterwards, HESI parameters were optimized together in order to obtain the highest intensity of most chromatographic peaks.

Table S1. Target list and list of labelled internal standards with synonyms, chemical groups and families(*).

Compound	Common synonims	CAS	Chemical group	Pesticide type
2,4,5-T		93-76-5	Aryloxyalkanoic acid	Herbicide
2,4,5-TP	Fenoprop, Silvex	93-72-1	Aryloxyalkanoic acid	Herbicide, Growth regulator
2,4-D		94-75-7	Aryloxyalkanoic acid	Herbicide, Growth regulator
2,4-DB		94-82-6	Aryloxyalkanoic acid	Herbicide
2-hydroxyatrazine		2163-68-0	Triazine	Herbicide
2-hydroxydesisopropylatrazine		7313-54-4	Metabolite	
2-hydroxyterbuthylazine		66753-07-9	Metabolite	
3-hydroxycarbofuran		16655-82-6	Metabolite	
Acetamiprid		135410-20-7	Neonicotinoid	Insecticide
Acetochlor		34256-82-1	Chloroacetamide	Herbicide
Aldicarb		116-06-3	Oxime carbamate	Acaricide, Nematicide, Insecticide
Atraton		1610-17-9	Triazine	Herbicide
Atrazine		1912-24-9	Triazine	Herbicide
Azinphos-methyl		86-50-0	Organophosphorous	Insecticide
Azoxystrobin		131860-33-8	Strobilurin	Fungicide
Bentazone		25057-89-0	Benzothiadiazinone	Herbicide
Bromoxynil		1689-84-5	Hydroxybenzonitrile	Herbicide
Carbaryl		63-25-2	Carbamate	Acaricide, Insecticide, Growth regulator
Carbendazim		10605-21-7	Benzimidazole	Fungicide
Carbofuran		1563-66-2	N-methyl-carbamate	Nematicide, Acaricide, Insecticide
Chlorfenvinphos		470-90-6	Organophosphorous	Insecticide, Acaricide
Chlorotoluron		15545-48-9	Urea	Herbicide
Chloroxuron		1982-47-4	Urea	Herbicide
Clothianidin		210880-92-5	Neonicotinoid	Insecticide
Crimidine		208-622-6	Pryimidinamine	Rodenticide

Cyanazine		21725-46-2	Triazine	Herbicide
Cybutryne	Irgarol	28159-98-0	Triazine	Algicide
Cycloxydim		101205-02-1	Cyclohexanedione oxime	Herbicide
Cyprodinil		121552-61-2	Anilinopyrimidine	Fungicide
Desethylatrazine	DEA	6190-65-4	metabolite	
Desethylterbuthylazine		30125-63-4	Triazine	
Desisopropylatrazine	DIA	1007-28-9	Metabolite	
Diazinon		333-41-5	Organophosphorous	Insecticide, Nematicide, Acaricide
Dichlorprop	2,4-DP	120-36-5	Aryloxyalkanoic acid	Herbicide, Growth regulator
Dimethoate	Omethoate	60-51-5	Organophosphorous	Insecticide, Acaricide
Diuron		330-54-1	Urea	Herbicide
Eptam	EPTC	759-94-4	Thiocarbamate	Herbicide
Fenuron		101-42-8	Urea	Herbicide
Flufenacet		142459-58-3	Oxyacetamide	Herbicide
Fluroxypyr		69377-81-7	Pyridinecarboxylic acids	Herbicide
Hexythiazox		78587-05-0	Carboxamide	Acaricide, Insecticide
Imidacloprid		138261-41-3	Neonicotinoid	Insecticide
Ioxynil		1689-83-4	Hydroxybenzonitrile	Herbicide
Isoprocarb		2631-40-5	Carbamate	Insecticide
Isoproturon		34123-59-6	Urea	Herbicide
Linuron		330-55-2	Urea	Herbicide
Malathion		121-75-5	Organophosphorous	Insecticide, Acaricide
MCPA		94-74-6	Aryloxyalkanoic acid	Herbicide
MCPB		94-81-5	Aryloxyalkanoic acid	Herbicide
MCPP	Mecoprop	93-65-2	Aryloxyalkanoic acid	Herbicide
Mesotrione		104206-82-8	Triketone	Herbicide
Metalaxyl		57837-19-1	Acylalanine	Fungicide
Metamitron		41394-05-2	Triazinone	Herbicide
Metazachlor		67129-08-2	Chloroacetamide	Herbicide
Methabenzthiazuron		18691-97-9	Urea	Herbicide

Methidathion		950-37-8	Organophosphorous	Insecticide, Acaricide
Methiocarb	Mercaptodimethur	2032-65-7	N-methyl-carbamate	Acaricide, Insecticide, Repellent, Molluscicide
Methomyl		16752-77-5	Oxime carbamate	Insecticide, Acaricide
Metobromuron		3060-89-7	Urea	Herbicide
Metolachlor		51218-45-2	Chloroacetamide	Herbicide
Metolachlor sulphonic acid		171118-09-5	Metabolite	
Metolcarb		1129-41-5	Carbamate	Insecticide
Metoxuron		19937-59-8	Urea	Herbicide
Metribuzin		21087-64-9	Triazinone	Herbicide
Mevinphos		7786-34-7	Organophosphorous	Insecticide, Acaricide
Monolinuron		1746-81-2	Urea	Herbicide
N,N-Diethyl-m-toluamide	DEET, Diethyltoluamide	134-62-3		Insecticide
Oxamyl		23135-22-0	Oxime carbamate	Nematicide, Insecticide, Acaricide
Paraoxon		311-45-5	Organophosphorous	Insecticide
Pencycuron		66063-05-6	Phenylurea	Fungicide
Pentachlorophenol		87-86-5	Organochlorine	Insecticide, Herbicide, Fungicide
Pethoxamid		106700-29-2	Chloroacetamide	Herbicide
Phenmediphan		13684-63-4	Bis-carbamate	Herbicide
Prochloraz		67747-09-5	Imidazole	Fungicide
Prometon	Pramitol	1610-18-0	Triazine	Herbicide
Prometryn		7287-19-6	Triazine	Herbicide
Propamocarb		24579-73-5	Carbamate	Fungicide
Propazine		139-40-2	Triazine	Herbicide
Propham		122-42-9	Carbamate	Fungicide, Growth regulator
Propiconazole		60207-90-1	Triazole	Fungicide
Propoxur		114-26-1	Carbamate	Insecticide
Propyzamide		23950-58-5	Benzamide	Herbicide
Prosulfocarb		52888-80-9	Thiocarbamate	Herbicide
Quinoxyfen		124495-18-7	Quinoline	Fungicide

Sebuthylazine	7286-69-3	Triazine	Herbicide
Simazine	122-34-9	Triazine	Herbicide
Sulcotrione	99105-77-8	Triketone	Herbicide
Tebuconazole	107534-96-3	Triazole	Fungicide
Tebuthiuron	34014-18-1	Urea	Herbicide
Terbuthylazine	5915-41-3	Triazine	Herbicide
Terbutryn	886-50-0	Triazine	Herbicide
Thiabendazole	148-79-8	Benzimidazole	Fungicide
Thiachloprid	111988-49-9	Neonicotinoid	Insecticide
Thiamethoxam	153719-23-4	Neonicotinoid	Insecticide
Thiodicarb	59669-26-0	Oxime carbamate	Molluscicide, Insecticide
Triclopyr	55335-06-3	Pyridinecarboxylic acids	Herbicide

(*) http://www.eurl-pesticides-datapool.eu/

Table S2. Historical data monitoring in the Llobregat, Ter and Besòs rivers, groundwater of Llobregat and Besòs rivers and drinking water avaible with analog sampling points and analytes within this study. Sampling points are described in Figure 1, as well of nomenclature literature references (Table 2). Literature references: (A) (Rivera et al., 1985), (B)(Rivera et al., 1986), (C) (Paune et al., 1998), (D) (Quintana et al., 2001), (E) (Rodriguez-Mozaz et al., 2004), (F) (Kampioti et al., 2005), (G) (Damásio et al., 2011), (H) (Kuster et al., 2008), (L) (Damásio et al., 2011), (M) (Köck-Schulmeyer et al., 2011), (O) (Köck-Schulmeyer et al., 2012), (P) (Proia et al., 2013), (Q) (Ginebreda et al., 2014).

(avg): results given in the former publication as a mean. (*): data obtained from graphical chart. Blank cells means non-analyzed compound for a particular study.

Literature reference	A	B	C	D	H	L	O	P	Q	H	Q
Sampling point	LLO-2									LLO-3	
Compounds	µg/L	µg/L	µg/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L
2,4-D					8.8-14.9				0.3	25.8-43.2	2.0
Atrazine	≈2-4·10^3	≈2·10^3		<LOQ			<LOQ-7.4	0.02-0.46	0.1		0.1
Desethylatrazine				<LOQ		0.53	<LOQ-5.8	0.17			
Desisopropylatrazine				<LOQ		151	<LOQ	4.2			
Bentazone									0.9		0.3
Chlorotoluron						<LOQ	<LOQ-10.3	0.03-0.59	0.3		1.2
Cyanazine				<LOQ			<LOQ-4.9	0.19	<LOQ		<LOQ
Diazinon						5.63	<LOQ-4.1	0.78-5.72	0.3		9.4
Dimethoate				<LOQ		1.48	<LOQ	0.49-1.06	<LOQ		1.0
Diuron						6.8	<LOQ-4.9	1.38-5.09	1.9		13.7
Isoproturon							<LOQ-81.6	0.01-0.6	0.2		0.2
Linuron						<LOQ	<LOQ	0.92	1.3		4.0
MCPA					16.9-81.2				1.6	27.2-134.1	20.3
MCPP					3.7-5.9				0.3	4.7-6.9	0.4
Metazachlor				<LOQ							
Metolachlor				<LOQ		5.27	<LOQ-6.6	0.13	<LOQ		<LOQ
metribuzine				<LOQ							
propazine				<LOQ							
Simazine				<LOQ-43		2.57	<LOQ-11.7	0.04-1.05	<LOQ		0.5
Terbuthylazine			0.09-1.2(avg)	<LOQ		141	<LOQ-32.9	0.04-65.74	1.2		6.1
Terbutryn				<LOQ-110							

Table S2 (continuation)

Literature reference	Q	H	Q	O	Q	H (*)	O
Sampling point	AN-1	AN-2		AN-3		RU-1	
Compounds	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L
2,4-D	0.165	76.1-108.9	2.23		1.79	≈9-28	
Atrazine	0.0128		<LOQ	<LOQ-0.9(avg)	0.297		<LOQ
Desethylatrazine				<LOQ			<LOQ
Desisopropylatrazine				<LOQ			<LOQ
Bentazone	0.323		0.473		0.295		
Chlorotoluron	0.19		<LOQ	<LOQ	<LOQ		<LOQ
Cyanazine	<LOQ		<LOQ	<LOQ	<LOQ		<LOQ
Diazinon	<LOQ		310	52(avg)	22.4		39 (avg)
Dimethoate	<LOQ		29.3	<LOQ-26.8	2.92		<LOQ-190
Diuron	0.225		42.1	23.3(avg)	11.8		461 (avg)-818 (max)
Isoproturon	1.96		1.07	<LOQ-2.9(avg)	0.358		<LOQ-1.7
Linuron	1.15		85.2	<LOQ	10.4		<LOQ
MCPA	0.153	45.5-63	0.32		0.678	≈46-63	
MCPP		2.2-5.2				≈3-6	
Metazachlor							
Metolachlor	<LOQ		<LOQ	<LOQ	1.84		<LOQ-6.1
metribuzine							
propazine	0.165		0.423		0.163		
Simazine	0.0338		0.234	<LOQ-1.7(avg)	1.8		
Terbuthylazine	0.963		1.19	8.2(avg)	0.17		
Terbutryn							

Table S2 (continuation)

Literature reference	D	E	F	H	L	M	O	P	Q
Sampling point	LLO-4								
Compounds	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L
2,4-D			6	30.8-68.6		0.2-6.7(avg)			0.9
Atrazine	<LOQ-29	5-463	7.8		1.65	1.2(avg)	<LOQ-10.2	0.04-0.43	0.3
Desethylatrazine	<LOQ	<LOQ-4	0.63		0.85	<LOQ	<LOQ-8.2	0.4-1.33	
Desisopropylatrazine	<LOQ-62		1.2		131	<LOQ	<LOQ	7.33-36.89	
Bentazone			<LOQ			<LOQ			2.9
Chlorotoluron			<LOQ		2.95	<LOQ-0.4(avg)	<LOQ-9.1	0.06-6.2	0.9
Cyanazine	<LOQ		0.4			<LOQ	<LOQ-8.6	0.25	<LOQ
Diazinon			8.4		26.2	17-34(avg)	<LOQ-132.3	7.1-79.03	17.0
Dimethoate	<LOQ-154		42		9.83	<LOQ	<LOQ-42.3	0.78-3.52	0.2
Diuron		<LOQ-239	9.5		21.6	10.5-36(avg)	<LOQ-41.4	10.53-31.13	54.0
Isoproturon		<LOQ-503	0.52			<LOQ-0.5(avg)	<LOQ-15.7	0.02-0.81	0.2
Linuron			<LOQ		6.23	<LOQ	<LOQ	1.17	0.1
MCPA			415	20.8-121.8		<LOQ			3.6
MCPP			0.88	2.8-4.2		<LOQ-2.9(avg)			1.3
Metazachlor	<LOQ								
Metolachlor	<LOQ		1.5		12.3	<LOQ	<LOQ-13.1	0.17-1.3	<LOQ
metribuzine	<LOQ								
propazine	<LOQ								
Simazine	<LOQ-84	8-2218	9.9		2.36	1.5-2.2(avg)	<LOQ-38.4	0.86-3.40	14.3
Terbuthylazine	<LOQ		12		124	18.6-44.6(avg)	<LOQ-81.5	0.05-82.84	2.4
Terbutryn	<LOQ-70								

Table S2 (continuation)

Literature reference	D	E	F	D
Sampling point	GW-LLO-2			GW-BES-1
Compounds	ng/L	ng/L	ng/L	ng/L
2,4-D			1.5	
Atrazine	<LOQ-25	7-14	2.3	<LOQ-59
Desethylatrazine	<LOQ		1.5	<LOQ-36
Desisopropylatrazine	<LOQ-25		1.1	<LOQ-63
Bentazone		2-3		
Chlorotoluron				
Cyanazine	<LOQ		1.33	
Diazinon			3.4	
Dimethoate	<LOQ			<LOQ
Diuron		4	3.7	
Isoproturon			1.4	
Linuron				
MCPA			2.8	
MCPP			0.71	
Metazachlor	<LOQ			
Metolachlor	<LOQ		3.3	
metribuzine	<LOQ			<LOQ
propazine	<LOQ			<LOQ
Simazine	<LOQ-73	22-153	54	46-164
Terbuthylazine	<LOQ-53		5.2	<LOQ-83
Terbutryn	<LOQ			<LOQ

Table S2 (continuation)

Literature reference	D	E	F	H	D	H	C	D	H
Sampling point	DWTP1				DWTP2		DWTP3		
Compounds	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	µg/L	ng/L	ng/L
2,4-D			2.1	2.2-4.2		3.8-4.7			6.8-7.9
Atrazine	<LOQ	<LOQ-18	0.82		31-62			<LOQ-25	
Desethylatrazine	<LOQ	<LOQ	<LOQ		<LOQ-33			<LOQ	
Desisopropylatrazine	<LOQ-25		<LOQ		<LOQ			<LOQ-73	
Bentazone			<LOQ						
Chlorotoluron			<LOQ						
Cyanazine	<LOQ		<LOQ		<LOQ			<LOQ	
Diazinon			1.4						
Dimethoate	<LOQ		<LOQ		<LOQ			<LOQ	
Diuron		<LOQ	<LOQ						
Isoproturon		<LOQ	<LOQ						
Linuron			<LOQ						
MCPA			28	<LOQ-26.1		3.3-4.7			16.2-67.2
MCPP			0.95	<LOQ-1.4		1.5-2.7			1.1-2.0
Metazachlor	<LOQ				<LOQ			<LOQ	
Metolachlor	<LOQ		<LOQ		<LOQ-40			<LOQ	
metribuzine	<LOQ				<LOQ			<LOQ	
propazine	<LOQ				<LOQ			<LOQ	
Simazine	<LOQ-43	5-82	6.9		<LOQ			<LOQ-34	
Terbuthylazine	<LOQ		6.7				0.14-0.80		
Terbutryn	<LOQ				<LOQ			<LOQ	

Table S3. Optimized parameters of the method. Guidelines for ion ratio, tolerance permitted and identification points are the values described in 2002/657/EC European Union Decision (EU, 2002) (not mandatory in water analysis).

Compound	Retention time	Surrogate	Polarity	Quantification transition	Voltage (eV)	Confirmation transition	Voltage (eV)	Ion Ratio ± tolerance	Tolerance permitted	Identification points
2,4,5-T	3.56	2,4-D-d3	ESI-	253>195	14	255>197	14	106 ± 21.1	± 20	5
2,4,5-TP	3.87	2,4-D-d3	ESI-	267>195	8	269>197	9	104 ± 20.7	± 20	5
2,4-D	3.18	2,4-D-d3	ESI-	221>163	11.5	219>161	11	81.9 ± 16.4	± 20	5
2,4-DB	3.70	2,4-D-d3	ESI-	247>161	5	249>163	6	53.4 ± 10.7	± 20	5
2-hydroxyatrazine	1.00	DIA-d5	ESI+	198>114	19	198>156	14	43 ± 10.8	± 25	4
2-hydroxydesisopropylatrazine	1.00	DIA-d5	ESI+	156>86	14	156>114	14	29.1 ± 7.3	± 25	4
2-hydroxyterbuthylazine	1.11	DIA-d5	ESI+	212>156	13	212>114	22	618 ± 185	± 30	4
3-hydroxycarbofuran	1.45	Carbofuran-d3	ESI+	238>181	8	238>163	11	75.7 ± 15.1	± 20	4
Acetamiprid	1.69	Imidacloprid-d4	ESI+	223>126	17	223>99	35	23.2 ± 5.8	± 25	4
Acetochlor	4.24	Chlorfenvinfos-d10	ESI+	270>224	10	270>148	16	66.2 ± 13.2	± 20	4
Aldicarb	2.26	Aldicarb-d3	ESI+	208>116	4.5	208>89	12.5	59.4 ± 11.9	± 20	4
Atraton	1.41	DIA-d5	ESI+	212>170	14	212>100	24	446 ± 111	± 25	4
Atrazine	3.05	Atrazine-d5	ESI+	216>174	15	216>104	24.5	32.4 ± 8.1	± 25	4
Azinphos-methyl	3.67	Diazinon-d10	ESI+	318>132	11	318>160	5	29.4 ± 7.4	± 25	4
Azoxystrobin	3.81	DEA-d6	ESI+	404>372	15	404>344	21	30.4 ± 7.6	± 25	4
Bentazone	2.99	2,4-D-d3	ESI-	239>197	18.5	239>132	23	37.7 ± 9.4	± 25	4
Bromoxynil	3.15	2,4-D-d3	ESI-	276>81	20.5	276>79	20.5	99.2 ± 19.8	± 20	4
Carbaryl	3.01	Carbofuran-d3	ESI+	202>145	7	202>127	26.5	44.7 ± 11.2	± 25	4
Carbendazim	1.00	Dimethoate-d6	ESI+	192>160	13	192>132	24	23.3 ± 5.8	± 25	4
Carbofuran	2.83	Carbofuran-d3	ESI+	222>165	9.5	222>123	17.5	107 ± 21.4	± 20	4
Chlorfenvinphos	4.38	Chlorfenvinfos-d10	ESI+	361>155	10	361>99	24	85.6 ± 17.1	± 20	4
Chlorotoluron	2.93	Isoproturon-d6	ESI+	213>72	16	213>46	13	29.7 ± 7.4	± 25	4
Chloroxuron	3.76	Diuron-d6	ESI+	291>72	12.5	291>218	24.5	3.3 ± 1.6	± 50	4
Clothianidin	1.47	Thiamethoxam-d4	ESI+	250>169	9	250>132	12	76.2 ± 15.2	± 20	4
Crimidine	1.64	DEA-d6	ESI+	172>136	17	172>107	23	61.1 ± 12.2	± 20	4
Cyanazine	2.44	Simazine-d5	ESI+	241>214	13	243>216	13	359 ± 89.8	± 25	5
Cybutryne	3.08	Atrazine-d5	ESI+	254>198	17	254>156	23	8.1 ± 4	± 50	4
Cycloxydim	4.99	Chlorfenvinfos-d10	ESI+	326>280	9	326>180	19	48.1 ± 12	± 25	4
Cyprodinil	3.43	Chlorfenvinfos-d10	ESI+	226>93	28	226>108	21.5	63.8 ± 12.8	± 20	4

Desethylatrazine	1.59	DEA-d6	ESI+	188>146	14	188>104	22	397 ± 99.2	± 25	4
Desethylterbuthylazine	2.50	Simazine-d5	ESI+	202>146	13	202>104	25	627 ± 188	± 30	4
Desisopropylatrazine	1.23	DIA-d5	ESI+	174>146	13	174>132	14	53.1 ± 10.6	± 20	4
Diazinon	4.65	Diazinon-d10	ESI+	305>169	19	305>97	29	32.7 ± 8.2	± 25	4
Dichlorprop	3.52	2,4-D-d3	ESI-	235>163	9	233>161	9	49.9 ± 12.5	± 25	5
Dimethoate	1.72	Dimethoate-d6	ESI+	230>125	19	230>199	8	97 ± 19.4	± 20	4
Diuron	3.16	Diuron-d6	ESI+	233>72	14	235>72	14	60.3 ± 12.1	± 20	5
Eptam	4.46	Methiocarb-d3	ESI+	190>128	11	190>86	15	47.7 ± 11.9	± 25	4
Fenuron	1.64	Isoproturon-d6	ESI+	165>72	17	165>46	12	239 ± 59.9	± 25	4
Flufenacet	4.21	Chlorfenvinfos-d10	ESI+	364>194	7	364>152	16	84 ± 16.8	± 20	4
Fluroxypyr	2.35	Dimethoate-d6	ESI-	255>197	10	253>195	10	156 ± 31.1	± 20	5
Hexythiazox	5.28	Chlorfenvinfos-d10	ESI+	353>228	14.5	353>168	23.5	78 ± 15.6	± 20	4
Imidacloprid	1.56	Imidacloprid-d4	ESI+	256>209	13.5	256>175	16.5	88.5 ± 17.7	± 20	4
Ioxynil	3.46	2,4-D-d3	ESI-	370>127	29	370>215	31	9.6 ± 4.8	± 50	4
Isoprocarb	3.29	Carbofuran-d3	ESI+	194>137	6	194>95	13	38.1 ± 9.5	± 25	4
Isoproturon	3.12	Isoproturon-d6	ESI+	207>72	11.5	207>165	12	11.4 ± 3.4	± 30	4
Linuron	3.73	Diuron-d6	ESI+	249>160	16	249>182	13.5	84.8 ± 17	± 20	4
Malathion	4.13	Diazinon-d10	ESI+	331>127	10	331>285	4	50.5 ± 10.1	± 20	4
MCPA	3.18	MCPA-d3	ESI-	199>141	13	201>143	13	257 ± 64.3	± 25	5
MCPB	3.72	MCPA-d3	ESI-	227>141	6	229>143	5	34.3 ± 8.6	± 25	5
MCPP	3.50	MCPA-d3	ESI-	213>141	11.5	213>71	9.5	4.1 ± 2	± 50	4
Mesotrione	2.62	Chlorfenvinfos-d10	ESI-	338>291	6	338>212	29	26.2 ± 6.6	± 25	4
Metalaxyl	3.13	Metalaxyl-13C6	ESI+	280>220	11	280>192	16	53.6 ± 10.7	± 20	4
Metamitron	1.45	Isoproturon-d6	ESI+	203>175	14.5	203>104	20	68.8 ± 13.8	± 20	4
Metazachlor	3.36	Diuron-d6	ESI+	278>134	18	278>210	8	144 ± 28.7	± 20	4
Methabenzthiazuron	2.84	Isoproturon-d6	ESI+	222>165	14	222>150	30	35.7 ± 8.9	± 25	4
Methidathion	3.70	Diazinon-d10	ESI+	303>85	17	303>145	6	54.6 ± 10.9	± 20	4
Methiocarb	3.67	Methiocarb-d3	ESI+	226>121	20	226>169	10	105 ± 21.1	± 20	4
Methomyl	1.23	Aldicarb-d3	ESI+	163>88	8	163>106	9.5	75.9 ± 15.2	± 20	4
Metobromuron	3.32	Isoproturon-d6	ESI+	259>148	13	259>170	15.5	76.5 ± 15.3	± 20	4
Metolachlor	4.22	Diuron-d6	ESI+	284>176	23.5	284>252	13	36 ± 9	± 25	4
Metolachlor sulphonic acid	1.52	Dimethoate-d6	ESI-	328>80	27	328>121	21	64 ± 12.8	± 20	4
Metolcarb	2.52	Aldicarb-d3	ESI+	166>109	10	166>94	28	23.5 ± 5.9	± 25	4
Metoxuron	2.16	Diuron-d6	ESI+	229>72	11.5	229>156	23	1311 ± 655	± 50	4
Metribuzin	2.64	Simazine-d5	ESI+	215>187	16	215>84	18	34.9 ± 8.7	± 25	4
Mevinphos	1.44	Dimethoate-d6	ESI+	225>193	4	225>127	13	146 ± 29.1	± 20	4

Monolinuron	3.17	Isoproturon-d6	ESI+	215>148	13	215>126	17	144 ± 28.7	± 20	4
N,N-Diethyl-m-toluamide	3.13	DEET-d7	ESI+	192>119	15	192>91	27	66.6 ± 13.3	± 20	4
Oxamyl	1.10	Aldicarb-d3	ESI+	237>72	9.5	237>90	6.5	28.8 ± 7.2	± 25	4
Paraoxon	3.22	Diazinon-d10	ESI+	276>220	16	276>174	21	65.2 ± 13	± 20	4
Pencycuron	4.71	Diuron-d6	ESI+	329>125	20	329>218	13.5	1226 ± 613	± 50	4
Pentachlorophenol	4.68	Pentachlorophenol-13C6	ESI-	265>35	20	263>263	0	2.9 ± 1.4	± 50	5
Pethoxamid	4.18	Chlorfenvinfos-d10	ESI+	296>131	17	296>250	8	66.3 ± 13.3	± 20	4
Phenmediphan	3.61	Carbofuran-d3	ESI+	318>168	11	318>136	20	166 ± 33.3	± 20	4
Prochloraz	3.68	Chlorfenvinfos-d10	ESI+	376>308	10.5	376>70	18	26.3 ± 6.6	± 25	4
Prometon	1.89	DIA-d5	ESI+	226>142	24	226>184	15	73.8 ± 14.8	± 20	4
Prometryn	2.87	Terbutryn-d5	ESI+	242>158	20	242>200	16	231 ± 57.9	± 25	4
Propamocarb	0.98	Carbofuran-d3	ESI+	189>102	13	189>74	23	29 ± 7.3	± 25	4
Propazine	3.55	Terbuthylazine-d5	ESI+	230>188	14	230>146	20	119 ± 23.9	± 20	4
Propham	3.43	Atrazine-d5	ESI+	180>138	4	180>120	13	58.9 ± 11.8	± 20	4
Propiconazole	4.31	Chlorfenvinfos-d10	ESI+	342>69	13	342>159	26	56.7 ± 11.3	± 20	4
Propoxur	2.75	Carbofuran-d3	ESI+	210>111	12	210>168	4	73.4 ± 14.7	± 20	4
Propyzamide	3.96	Chlorfenvinfos-d10	ESI+	256>190	11	256>173	19	49.8 ± 12.4	± 25	4
Prosulfocarb	5.00	Methiocarb-d3	ESI+	252>91	20	252>128	10	28.7 ± 7.2	± 25	4
Quinoxyfen	5.04	Chlorfenvinfos-d10	ESI+	308>162	45	308>197	27	63.8 ± 12.8	± 20	4
Sebuthylazine	3.50	Terbuthylazine-d5	ESI+	230>174	16	230>104	28	21.4 ± 5.3	± 25	4
Simazine	2.41	Simazine-d5	ESI+	202>124	13.5	202>132	15.5	94.8 ± 19	± 20	4
Sulcotrione	2.74	DEET-d7	ESI-	327>291	7	327>212	28	21.3 ± 5.3	± 25	4
Tebuconazole	4.03	Chlorfenvinfos-d10	ESI+	308>70	13	308>125	32	9.3 ± 4.6	± 50	4
Tebuthiuron	2.05	Isoproturon-d6	ESI+	229>172	14	229>116	24	24.7 ± 6.2	± 25	4
Terbuthylazine	3.66	Terbuthylazine-d5	ESI+	230>174	14	230>104	29	16 ± 4.8	± 30	4
Terbutryn	2.90	Terbutryn-d5	ESI+	242>186	16	242>96	26	701 ± 210	± 30	4
Thiabendazole	1.00	Dimethoate-d6	ESI+	202>175	19.5	202>131	27	12.8 ± 3.8	± 30	4
Thiachloprid	2.10	DIA-d5	ESI+	253>126	18	255>128	18	71.2 ± 14.2	± 20	5
Thiamethoxam	1.28	Thiamethoxam-d4	ESI+	292>211	11.5	292>181	18	33.2 ± 8.3	± 25	4
Thiodicarb	2.58	Aldicarb-d3	ESI+	355>88	8.5	355>108	11.5	61.4 ± 12.3	± 20	4
Triclopyr	3.35	2,4-D-d3	ESI-	254>196	11	256>198	8	110 ± 22.1	± 20	5

2,4-D-d3	3.17		ESI-	222>164	9
Aldicarb-d3	2.24		ESI+	216>89	14

Atrazine-d5	3.04		ESI+	221>179	15
Carbofuran-d3	2.79		ESI+	225>165	8
Chlorfenvinfos-d10	4.36		ESI+	369>165	10
DEA-d6	1.57		ESI+	194>147	15
DEET-d7	3.11		ESI+	199>126	16
DIA-d5	1.20		ESI+	179>137	15
Diazinon-d10	4.62		ESI+	315>170	19
Dimethoate-d6	1.77		ESI+	236>205	6
Diuron-d6	3.13		ESI+	239>78	16
Imidacloprid-d4	1.56		ESI+	260>213	12
Isoproturon-d6	3.10		ESI+	213>78	16
MCPA-d3	3.17		ESI-	204>146	11
Metalaxyl-13C6	3.13		ESI+	286>226	11
Methiocarb-d3	3.66		ESI+	229>169	6
Pentachlorophenol-13C6	4.68		ESI-	271>271	0
Simazine-d5	2.38		ESI+	207>137	16
Terbuthylazine-d5	3.65		ESI+	235>179	15
Terbutryn-d5	2.86		ESI+	247>159	23
Thiamethoxam-d4	1.26		ESI+	296>215	9

Table S4. Quality parameters of the method.

Compound	Meets validation objectives?	Linearity (r^2)	LOD (ng/L)	LOQ(*) (ng/L)	Accuracy at LOD (%)	Precision at LOD (%)	Expanded uncertainty at LOD (%)	Declared uncertainty of the method (%)
2,4,5-T	yes	0.9976	0.5	5	-8.7	20	44	20
2,4,5-TP	yes	0.9996	0.25	5	-13.8	20.6	50	40
2,4-D	yes	0.9975	0.5	15	11.5	6.6	26	30
2,4-DB	yes	0.9982	1	15	8.4	16	36	40
2-hydroxyatrazine		0.9982	10	25				-
2-hydroxydesisopropylatrazine		0.9985	10	25				-
2-hydroxyterbuthylazine		0.9990	1	25				-
3-hydroxycarbofuran		0.9994	5	25	-18.9	30.5		-
Acetamiprid	yes	0.9990	1	5	13.3	22.7	53	40
Acetochlor		0.9982	5	25	42.5	33.4		-
Aldicarb	yes	0.9973	10	15	17.9	15.6	47	50
Atraton	yes	0.9991	1	5	-3.1	22.2	45	40
Atrazine	yes	0.9997	0.25	5	-1.8	5.2	11	20
Azinphos-methyl	yes	0.9992	2.5	25	-15.9	18.6	47	60
Azoxystrobin	yes	0.9985	0.25	5	5	18.3	38	45
Bentazone	yes	0.9975	0.25	5	-16.4	18.9	50	40
Bromoxynil		0.9983	1	25				-
Carbaryl	yes	0.9981	0.25	15	-17.7	24	60	60
Carbendazim		0.9994	0.25	25				-
Carbofuran	yes	0.9988	0.25	5	-6	4.9	16	20
Chlorfenvinphos	yes	0.9992	1	5	10.6	20.3	46	30
Chlorotoluron	yes	0.9996	1	5	-0.6	11.2	22	30
Chloroxuron	yes	0.9989	0.5	5	4	16.4	34	30
Clothianidin		0.9993	10	25				-
Crimidine	yes	0.9995	2.5	5	1.7	16	32	50
Cyanazine	yes	0.9989	0.25	5	-6.1	7.5	19	40
Cybutryne	yes	0.9993	0.25	5	-8.5	13.2	31	40
Cycloxydim		0.9981	1	25				-
Cyprodinil	yes	0.9970	2.5	5	-20.3	22.7	61	60
Desethylatrazine	yes	0.9995	2.5	5	-3.2	12.6	26	25
Desethylterbuthylazine	yes	0.9998	0.5	5	9.7	18.2	41	30
Desisopropylatrazine		0.9975	10	25				-
Diazinon	yes	0.9998	0.25	5	-5	7.9	19	30
Dichlorprop		0.9985	0.25	25				-
Dimethoate	yes	0.9993	1	5			22	30
Diuron	yes	0.9991	0.5	15	-6.5	11.3	26	40
Eptam	yes	0.9983	2.5	5	20.5	17	53	40
Fenuron		0.9983	1	25				-
Flufenacet	yes	0.9984	0.5	5	-5.9	19.7	41	40
Fluroxypyr	yes	0.9993	2.5	5	1.8	15.9	32	40
Hexythiazox	yes	0.9993	5	15	-20	13.4	49	60
Imidacloprid	yes	0.9994	1	5	5.8	22.1	46	30
Ioxynil		0.9982	0.25	25				-
Isoprocarb	yes	0.9995	0.5	5	-11.2	14.3	36	40
Isoproturon	yes	0.9998	0.25	5	-6.7	17.6	38	35
Linuron	yes	0.9984	5	15	0.6	18.8	38	50
Malathion		0.9985	1	5	-14.4	24.9		-
MCPA	yes	0.9996	1	5	1.8	20.3	41	15

MCPB	yes	0.9969	2.5	5	-2.2	22.4	45	40
MCPP	yes	0.9987	0.25	15	2.2	14.2	29	40
Mesotrione		0.9992	5	25				-
Metalaxyl	yes	0.9991	0.25	5	-2.3	9.9	20	30
Metamitron	yes	0.9974	5	25	-1.8	16.6	33	50
Metazachlor	yes	0.9991	0.25	5	-5.2	22.1	46	50
Methabenzthiazuron	yes	0.9986	0.25	5	-3.8	9	20	30
Methidathion		0.9985	1	25				
Methiocarb	yes	0.9992	0.25	5			52	60
Methomyl		0.9986	5	25				-
Metobromuron	yes	0.9993	2.5	5	7.6	13.7	31	30
Metolachlor	yes	0.9988	0.25	15	20.4	17.7	54	60
Metolachlor sulphonic acid	yes	0.9974	5	15	15.3	22.2	54	60
Metolcarb		0.9989	2.5	25	32.1	22.2		-
Metoxuron	yes	0.9981	1	5	-15.2	25.1	59	60
Metribuzin	yes	0.9994	1	5	-1.9	10.8	22	40
Mevinphos	yes	0.9994	2.5	5	13.5	17.1	44	40
Monolinuron	yes	0.9992	1	5	2	11.3	23	30
N,N-Diethyl-m-toluamide		0.9993	0.25	25				-
Oxamyl		0.9987	5	25				-
Paraoxon	yes	0.9997	0.5	5	-13.4	14.6	40	50
Pencycuron	yes	0.9990	2.5	5	15.9	21.6	54	50
Pentachlorophenol		0.9988	15	25				-
Pethoxamid	yes	0.9981	0.25	5	-11.7	17.9	43	50
Phenmediphan		0.9959	0.5	25				-
Prochloraz	yes	0.9997	0.5	25	-4.2	25.8	47	50
Prometon	yes	0.9997	0.5	5	3.8	20.1	41	45
Prometryn	yes	0.9987	1	5	-6.2	7.3	19	30
Propamocarb		0.9979	5	25	-39.6	25.1		-
Propazine	yes	0.9996	0.25	5	-3	6.1	14	25
Propham	yes	0.9989	2.5	15	-18.6	15.8	49	60
Propiconazole	yes	0.9996	0.5	5	1.8	21.5	43	30
Propoxur	yes	0.9997	0.5	5	-0.6	8.1	16	30
Propyzamide	yes	0.9986	0.5	5	-9.6	17.8	40	50
Prosulfocarb	yes	0.9984	0.5	5	8.4	23.5	50	50
Quinoxyfen		0.9975	2.5	25	-23.3	23.8		-
Sebuthylazine	yes	0.9994	0.25	5	-7.7	4.9	18	30
Simazine	yes	0.9996	1	5	-0.7	6	12	25
Sulcotrione	yes	0.9995	2.5	5	-11.2	18.5	43	35
Tebuconazole	yes	0.9992	0.25	5	-11.6	12.9	35	40
Tebuthiuron	yes	0.9996	0.25	5	-5.8	13.9	30	35
Terbuthylazine	yes	0.9991	0.25	5	4	15.2	31	25
Terbutryn	yes	0.9993	0.25	5	-6.6	6	18	30
Thiabendazole		0.9978	0.25	25				-
Thiachloprid	yes	0.9985	1	5	-9.4	16.9	39	60
Thiamethoxam		0.9991	5	25				-
Thiodicarb		0.9988	2.5	25				-
Triclopyr	yes	0.9989	5	5	6.5	23.8	49	50

(*) LOQ was set at generic 25 ng/L for compounds that not meet the objectives of the accreditation.

Table S5. Matrix effect as a % of signal enhancement (% > 0) or signal supression (% < 0). Signal suppression was evaluated in all matrices as described elsewhere (Boleda et al., 2013) comparing the response (areas) of the matrix blank versus the responses of the matrix and ultrapure water spiked both at 125 ng/L.

	surface water	**groundwater**	**tap water**		**surface water**	**groundwater**	**tap water**		**surface water**	**groundwater**	**tap water**
2,4,5-T	-1	10	-2	Diazinon	1	93	-13	Mevinphos	12	0	-6
2,4,5-TP	-3	16	-12	Dichlorprop	-2	11	-7	Monolinuron	9	-2	7
2,4-D	9	7	-1	Dimethoate	20	5	12	N,N-Diethyl-m-toluamide	9	7	5
2,4-DB	8	16	0	Diuron	8	0	14	Oxamyl	29	-7	9
2-hydroxyatrazine	19	14	1	Eptam	2	2	8	Paraoxon	-1	0	6
2-hydroxydesisopropylatrazine	28	-9	35	Fenuron	58	33	55	Pencycuron	-5	12	3
2-hydroxyterbuthylazine	-6	-9	-5	Flufenacet	3	6	14	Pentachlorophenol	-5	28	-10
3-hydroxycarbofuran	32	-2	16	Fluroxypyr	21	8	13	Pethoxamid	-3	5	1
Acetamiprid	19	7	18	Hexythiazox	-3	28	8	Phenmediphan	100	1	100
Acetochlor	-3	3	8	Imidacloprid	15	6	12	Prochloraz	-9	-64	20
Aldicarb	16	10	30	Ioxynil	1	9	-26	Prometon	4	-3	5
Atraton	5	1	1	Isoprocarb	2	0	14	Prometryn	-2	-7	8
Atrazine	11	1	7	Isoproturon	8	8	5	Propamocarb	-29	-14	-50
Azinphos-methyl	-5	12	-3	Linuron	5	6	10	Propazine	5	1	7
Azoxystrobin	1	16	10	Malathion	13	13	16	Propham	10	-2	8
Bentazone	-5	5	-14	MCPA	8	9	-5	Propiconazole	1	5	4
Bromoxynil	4	4	-1	MCPB	11	14	-6	Propoxur	13	1	5
Carbaryl	30	1	35	MCPP	5	9	-9	Propyzamide	5	5	3
Carbendazim	19	17	1	Mesotrione	1	7	-8	Prosulfocarb	1	18	7
Carbofuran	12	1	10	Metalaxyl	0	0	-2	Quinoxyfen	-1	-161	-3
Chlorfenvinphos	2	10	-29	Metamitron	25	10	15	Sebuthylazine	3	4	5
Chlorotoluron	8	3	15	Metazachlor	3	2	4	Simazine	10	1	7
Chloroxuron	-2	7	-1	Methabenzthiazuron	12	1	11	Sulcotrione	4	10	-2
Clothianidin	28	11	28	Methidathion	10	-5	-14	Tebuconazole	-2	0	2
Crimidine	6	20	-4	Methiocarb	23	2	32	Tebuthiuron	13	7	8
Cyanazine	14	9	12	Methomyl	22	15	23	Terbuthylazine	9	2	8
Cybutryne	-5	-9	5	Metobromuron	6	4	15	Terbutryn	-2	-15	2
Cycloxydim	-22	53	100	Metolachlor	-4	4	15	Thiabendazole	3	14	24
Cyprodinil	-2	-21	3	Metolachlor sulphonic acid	23	11	12	Thiachloprid	23	6	24
Desethylatrazine	10	0	3	Metolcarb	16	2	14	Thiamethoxam	32	16	40
Desethylterbuthylazine	13	5	9	Metoxuron	23	27	24	Thiodicarb	-18	-1	-17
Desisopropylatrazine	17	5	18	Metribuzin	13	3	8	Triclopyr	1	3	0

Table S6. Concentrations of pesticides (ng/L) found in the Llobregat River basin during 2016-2017. Sampling points are shown in Figure 1. No data for a certain year or compound means that for that year the compound was not detected below its limit of quantification. For the compound list of the method, see Table S1. When for a certain compound and year only one positive is found, the Mean is the concentration value for that compound. For the calculation of the medians, concentrations below LOQ were defined as 1/2 LOQ.

Sampling point	LLO-1						
		samples (n) frequency (f %)	Concentration (ng/L) in positive samples				
	year	(positives)	Min	Max	Median	Average	Cases >100 ng/L
2,4-D	2016	n=7 f=14 % (1)		23	<LOQ	<LOQ	
	2017	n=6 f=17 % (1)		41	<LOQ	19	
Carbendazim	2016	n=7 f=43 % (3)	28	1054	<LOQ	167	1
Chlorotoluron	2017	n=6 f=50 % (3)	7	228	10	82	1
Diazinon	2016	n=7 f=14 % (1)		6	<LOQ	<LOQ	
Dimethoate	2016	n=7 f=14 % (1)		7	<LOQ	<LOQ	
Imidacloprid	2017	n=6 f=50 % (3)	5	8	5	6	
Isoproturon	2017	n=6 f=17 % (1)		12	<LOQ	6	
MCPA	2016	n=7 f=14 % (1)		62	<LOQ	11	
	2017	n=6 f=17 % (1)		37	<LOQ	14	
Metazachlor	2016	n=7 f=14 % (1)		43	<LOQ	8	
	2017	n=6 f=17 % (1)		9	<LOQ	5	
Propamocarb	2016	n=7 f=14 % (1)		46	<LOQ	<LOQ	
Propiconazole	2016	n=7 f=14 % (1)		11	<LOQ	<LOQ	
	2017	n=6 f=50 % (3)	5	83	10	33	
Prosulfocarb	2016	n=7 f=14 % (1)		11	<LOQ	<LOQ	
Terbutryn	2016	n=7 f=14 % (1)		5	<LOQ	<LOQ	
	2017	n=6 f=17 % (1)		24	<LOQ	10	

Sampling point	CA-1						
		samples (n) frequency (f %)	Concentration (ng/L) in positive samples				
	year	(positives)	Min	Max	Median	Average	Cases >100 ng/L
2,4-D	2017	n=6 f=33 % (2)	20	32	<LOQ	17	
Chlorotoluron	2017	n=6 f=50 % (3)	5	8	7	7	
Isoproturon	2017	n=6 f=33 % (2)	7	8	5	5	
Prosulfocarb	2016	n=7 f=43 % (3)	5	34	<LOQ	11	
	2017	n=6 f=50 % (3)	6	17	8	9	

Sampling point	CA-2						
		samples (n) frequency (f %)	Concentration (ng/L) in positive samples				
	year	(positives)	Min	Max	Median	Average	Cases >100 ng/L
Carbendazim	2016	n=7 f=29 % (2)	33	94	<LOQ	27	
Chlorotoluron	2017	n=6 f=17 % (1)		5	<LOQ	<LOQ	
DEET	2016	n=7 f=14 % (1)		28	<LOQ	<LOQ	
Imidacloprid	2016	n=7 f=29 % (2)	11	20	<LOQ	6	
	2017	n=6 f=67 % (4)	9	31	12	16	
Isoproturon	2016	n=7 f=14 % (1)		6	<LOQ	<LOQ	
	2017	n=6 f=17 % (1)		12	<LOQ	5	
MCPP	2016	n=7 f=14 % (1)		22	<LOQ	<LOQ	
Metazachlor	2016	n=7 f=14 % (1)		6	<LOQ	<LOQ	
Propiconazole	2017	n=6 f=17 % (1)		5	<LOQ	<LOQ	
Prosulfocarb	2016	n=7 f=29 % (2)	6	15	<LOQ	5	

	2017	n=6 f=17 % (1)		17	<LOQ	6	
Tebuconazole	2016	n=7 f=14 % (1)		5	<LOQ	<LOQ	
	2017	n=6 f=17 % (1)		6	<LOQ	<LOQ	
Terbutryn	2017	n=6 f=17 % (1)		5	<LOQ	<LOQ	

Sampling point	LLO-2						
		samples (n) frequency (f %)	Concentration (ng/L) in positive samples				
	year	(positives)	Min	Max	Median	Average	Cases >100 ng/L
2,4-D	2017	n=6 f=17 % (1)		21	<LOQ	<LOQ	
Carbendazim	2016	n=7 f=71 % (5)	29	269	36	65	
Chlorotoluron	2017	n=6 f=17 % (1)		8	<LOQ	<LOQ	
DEET	2017	n=6 f=17 % (1)		33	<LOQ	<LOQ	
Diazinon	2016	n=7 f=29 % (2)	11	71	<LOQ	13	
	2017	n=6 f=17 % (1)		16	<LOQ	5	
Dimethoate	2016	n=7 f=14 % (1)	12	12	<LOQ	<LOQ	
Imidacloprid	2016	n=7 f=29 % (2)	5	9	<LOQ	<LOQ	
	2017	n=6 f=17 % (1)		16	<LOQ	5	
Isoproturon	2016	n=7 f=29 % (2)	5	5	<LOQ	<LOQ	
	2017	n=6 f=17 % (1)		9	<LOQ	<LOQ	
Metazachlor	2016	n=7 f=14 % (1)		46	<LOQ	9	
Propiconazole	2017	n=6 f=33 % (2)	8	82	<LOQ	17	
Prosulfocarb	2016	n=7 f=29 % (2)	5	13	<LOQ	<LOQ	
	2017	n=6 f=17 % (1)		5	<LOQ	<LOQ	
Terbutryn	2016	n=7 f=43 % (3)	5	19	<LOQ	6	
	2017	n=6 f=17 % (1)		15	<LOQ	5	

Sampling point	AN-1						
		samples (n) frequency (f %)	Concentration (ng/L) in positive samples				
	year	(positives)	Min	Max	Median	Average	Cases >100 ng/L
2,4-D	2016	n=7 f=29 % (2)	15	26	<LOQ	<LOQ	
	2017	n=4 f=75 % (3)	22	855	26	229	1
Chlorotoluron	2017	n=4 f=50 % (2)	9	12	6	7	
Imidacloprid	2016	n=7 f=29 % (2)	15	21	<LOQ	7	
	2017	n=4 f=100 % (4)	6	12	10	10	
Isoproturon	2017	n=4 f=25 % (1)		10	<LOQ	<LOQ	
Prosulfocarb	2016	n=7 f=86 % (6)	5	104	7	23	
	2017	n=4 f=75 % (3)	5	9	6	6	
Tebuconazole	2016	n=7 f=29 % (2)	6	9	<LOQ	<LOQ	

Sampling point	AN-2						
		samples (n) frequency (f %)	Concentration (ng/L) in positive samples				
	year	(positives)	Min	Max	Median	Average	Cases >100 ng/L
2,4-D	2016	n=7 f=57 % (4)	25	152	25	49	
	2017	n=6 f=83 % (5)	19	102	38	44	1
Acetamiprid	2017	n=6 f=17 % (1)		6	<LOQ	<LOQ	
Carbendazim	2016	n=7 f=100 % (7)	235	9574	2623	4053	
	2017	n=6 f=50 % (3)	144	2830	78	905	3
Chlorotoluron	2016	n=7 f=14 % (1)	12	12	<LOQ	<LOQ	
	2017	n=6 f=33 % (2)	12	27	<LOQ	8	
Cybutrine	2016	n=7 f=14 % (1)		5	<LOQ	<LOQ	
DEET	2016	n=7 f=57 % (4)	67	191	67	73	
	2017	n=6 f=50 % (3)	48	190	30	62	1
Diazinon	2016	n=7 f=100 % (7)	5	131	20	35	

	2017	n=6 f=100 % (6)	5	104	15	33	1
Dimethoate	2016	n=7 f=29 % (2)	69	226	<LOQ	44	
	2017	n=6 f=50 % (3)	5	415	<LOQ	74	1
Diuron	2016	n=7 f=86 % (6)	17	135	41	59	
	2017	n=6 f=83 % (5)	17	68	33	38	
Fenuron	2016	n=7 f=29 % (2)	68	90	<LOQ	31	
Imidacloprid	2016	n=7 f=86 % (6)	20	361	149	131	
	2017	n=6 f=67 % (4)	88	165	91	80	2
Isoproturon	2016	n=7 f=29 % (2)	5	36	<LOQ	8	
	2017	n=6 f=33 % (2)	14	16	<LOQ	7	
MCPA	2017	n=6 f=17 % (1)		32			
MCPP	2016	n=7 f=57 % (4)	5	32	<LOQ	<LOQ	
	2017	n=6 f=17 % (1)		33	<LOQ	<LOQ	
Metalaxyl	2016	n=7 f=14 % (1)		17	<LOQ	5	
Metazachlor	2017	n=6 f=17 % (1)		14	<LOQ	<LOQ	
Propiconazole	2016	n=7 f=71 % (5)	11	36	12	18	
	2017	n=6 f=83 % (5)	11	204	13	45	1
Propoxur	2017	n=6 f=17 % (1)		5	5	5	
Prosulfocarb	2016	n=7 f=57 % (4)	11	364	11	76	
	2017	n=6 f=67 % (4)	6	32	8	10	
Tebuconazole	2016	n=7 f=71 % (5)	5	9	5	5	
	2017	n=6 f=100 % (6)	5	12	7	8	
Terbuthylazine-desethyl	2016	n=7 f=14 % (1)		6	<LOQ	<LOQ	
Terbutryn	2016	n=7 f=100 % (7)	5	35	24	22	
	2017	n=6 f=100 % (6)	11	154	17	39	1

Sampling point	AN-3						
		samples (n) frequency (f %) (positives)	Concentration (ng/L) in positive samples				
	year		Min	Max	Median	Average	Cases >100 ng/L
2,4-D	2016	n=7 f=14 % (1)		33			
	2017	n=6 f=50 % (3)	17	36	<LOQ	18	
Acetamiprid	2017	n=6 f=50 % (3)	6	11	<LOQ	5	
Atrazine	2016	n=7 f=14 % (1)		5			
Bentazone	2016	n=7 f=57 % (4)	7	507	7	91	
	2017	n=6 f=83 % (5)	9	42	20	21	
Carbendazim	2016	n=7 f=100 % (7)	125	16866	1990	4843	
	2017	n=6 f=50 % (3)	258	2771	258	843	3
Chlorotoluron	2016	n=7 f=14 % (1)		6			
	2017	n=6 f=33 % (2)	7	33	<LOQ	8	
DEET	2016	n=7 f=57 % (4)	40	174	40	67	
	2017	n=6 f=67 % (4)	40	95	53	52	
Diazinon	2016	n=7 f=29 % (2)	5	8	<LOQ	<LOQ	
	2017	n=6 f=50 % (3)	5	53	<LOQ	14	
Dimethoate	2016	n=7 f=14 % (1)		10			
	2017	n=6 f=17 % (1)		12			
Diuron	2016	n=7 f=86 % (6)	16	70	27	30	
	2017	n=6 f=100 % (6)	16	47	22	27	
Fenuron	2016	n=7 f=14 % (1)		25			
Imidacloprid	2016	n=7 f=100 % (7)	12	447	59	115	
	2017	n=6 f=100 % (6)	24	215	62	81	1
Isoproturon	2016	n=7 f=29 % (2)	15	148	<LOQ	25	
	2017	n=6 f=50 % (3)	6	7	<LOQ	5	
MCPP	2016	n=7 f=57 % (4)	6	40	<LOQ	15	
	2017	n=6 f=17 % (1)		16			
Metalaxyl	2016	n=7 f=86 % (6)	6	61	10	21	
	2017	n=6 f=67 % (4)	6	34	6	11	
Metazachlor	2016	n=7 f=14 % (1)		11			

Methiocarb	2016	n=7 f=29 % (2)	5	21	<LOQ	5	
	2017	n=6 f=17 % (1)		7			
Propiconazole	2016	n=7 f=57 % (4)	5	13	5	6	
	2017	n=6 f=83 % (5)	7	182	8	38	
Propoxur	2016	n=7 f=71 % (5)	5	10	6	6	1
	2017	n=6 f=17 % (1)		6			
Prosulfocarb	2016	n=7 f=86 % (6)	8	123	13	32	
	2017	n=6 f=50 % (3)	9	30	6	10	
Simazine	2016	n=7 f=57 % (4)	30	456	30	91	
	2017	n=6 f=67 % (4)	6	16	7	8	
Tebuconazole	2016	n=7 f=71 % (5)	6	16	8	8	
	2017	n=6 f=100 % (6)	8	26	11	14	
Terbuthylazine	2017	n=6 f=17 % (1)		13			
Terbuthylazine-2-hydroxy	2016	n=7 f=29 % (2)	30	43	13	19	
Terbuthylazine-desethyl	2017	n=6 f=17 % (1)		13			
Terbutryn	2016	n=7 f=57 % (4)	6	12	6	7	
	2017	n=6 f=100 % (6)	5	59	9	17	

Sampling point	LLO-3						
		samples (n) frequency (f %)	Concentration (ng/L) in positive samples				
	year	(positives)	Min	Max	Median	Average	Cases >100 ng/L
Bentazone	2016	n=1 f=100 % (1)		13			
Diazinon	2016	n=1 f=100 % (1)		5			
Dimethoate	2016	n=1 f=100 % (1)		10			
Terbutryn	2016	n=1 f=100 % (1)		9			

Sampling point	RU-1						
		samples (n) frequency (f %)	Concentration (ng/L) in positive samples				
	year	(positives)	Min	Max	Median	Average	Cases >100 ng/L
2,4-D	2016	n=7 f=71 % (5)	15	36	16	18	
Acetamiprid	2016	n=7 f=29 % (2)	11	15	<LOQ	6	
	2017	n=6 f=33 % (2)	13	14	<LOQ	6	
Bentazone	2016	n=7 f=14 % (1)		10			
Carbendazim	2016	n=7 f=100 % (7)	127	545	198	259	
	2017	n=6 f=33 % (2)	43	297	<LOQ	65	1
Chlorotoluron	2017	n=6 f=33 % (2)	18	59	<LOQ	15	
DEET	2016	n=7 f=100 % (7)	58	753	138	280	
	2017	n=6 f=100 % (6)	129	656	178	301	6
Diazinon	2016	n=7 f=86 % (6)	19	148	31	44	
	2017	n=6 f=100 % (6)	13	186	27	74	2
Dimethoate	2016	n=7 f=29 % (2)	8	49	<LOQ	10	
	2017	n=6 f=67 % (4)	6	33	8	12	
Diuron	2016	n=7 f=100 % (7)	280	2127	805	928	
	2017	n=6 f=100 % (6)	171	530	292	312	6
Imidacloprid	2016	n=7 f=71 % (5)	58	208	77	80	
	2017	n=6 f=83 % (5)	71	193	119	113	5
Isoproturon	2016	n=7 f=14 % (1)		8			
	2017	n=6 f=67 % (4)	20	136	21	37	1
MCPA	2016	n=7 f=29 % (2)	34	46	<LOQ	13	
	2017	n=6 f=33 % (2)	34	126	<LOQ	28	1
MCPP	2016	n=7 f=86 % (6)	7	34	15	17	
	2017	n=6 f=17 % (1)		20			
Metolachlor	2017	n=6 f=17 % (1)		58			
Propamocarb	2016	n=7 f=14 % (1)		31			
Propiconazole	2016	n=7 f=100 % (7)	86	580	254	276	

	2017	n=6 f=100 % (6)	86	2216	274	578	4
Propoxur	2016	n=7 f=43 % (3)	8	10	<LOQ	5	
	2017	n=6 f=83 % (5)	6	15	7	8	
Propyzamide	2016	n=7 f=14 % (1)		36			
Tebuconazole	2016	n=7 f=100 % (7)	21	156	46	60	
	2017	n=6 f=100 % (6)	20	52	36	37	
Terbuthylazine-2-hydroxy	2016	n=7 f=14 % (1)		26			
Terbutryn	2016	n=7 f=100 % (7)	58	494	95	149	
	2017	n=6 f=100 % (6)	55	90	78	75	

Sampling point	LLO-4						
		samples (n) frequency (f %) (positives)	Concentration (ng/L) in positive samples				
	year		Min	Max	Median	Average	Cases >100 ng/L
2,4-D	2016	n=55 f=13 % (7)	15	58	<LOQ	<LOQ	
	2017	n=14 f=7 % (1)		47	<LOQ	<LOQ	
Acetamiprid	2016	n=55 f=2 % (1)		8	<LOQ	<LOQ	
	2017	n=14 f=7 % (1)		8	<LOQ	<LOQ	
Azoxystrobin	2016	n=55 f=2 % (1)		6	<LOQ	<LOQ	
Bentazone	2016	n=55 f=13 % (7)	6	17	<LOQ	<LOQ	
	2017	n=14 f=14 % (2)		16	<LOQ	<LOQ	
Carbendazim	2016	n=55 f=96 % (53)	36	1425	92	211	26
	2017	n=14 f=71 % (10)	40	568	49	109	6
Chlorotoluron	2017	n=14 f=29 % (4)	5	22	<LOQ	5	
DEET	2016	n=55 f=62 % (34)	25	154	32	33	1
	2017	n=14 f=21 % (3)			<LOQ	<LOQ	
Diazinon	2016	n=55 f=64 % (35)	5	17	6	6	
	2017	n=14 f=64 % (9)	5	32	7	9	
Dimethoate	2016	n=55 f=11 % (6)	7	21	<LOQ	<LOQ	
	2017	n=14 f=7 % (1)		16	<LOQ	<LOQ	
Diuron	2016	n=55 f=29 % (16)	15	232	8	16	1
	2017	n=14 f=29 % (4)	15	67	8	16	
Fenuron	2016	n=55 f=2 % (1)		34	<LOQ	<LOQ	
	2017	n=14 f=14 % (2)	30	43	<LOQ	<LOQ	
Imidacloprid	2016	n=55 f=80 % (44)	7	36	11	11	
	2017	n=14 f=93 % (13)	6	86	10	16	
Isoproturon	2016	n=55 f=18 % (10)	5	16	<LOQ	<LOQ	
	2017	n=14 f=14 % (2)		13	<LOQ	<LOQ	
Linuron	2016	n=55 f=4 % (2)	20	24	<LOQ	<LOQ	
MCPA	2016	n=55 f=5 % (3)	25	61	<LOQ	5	
MCPP	2016	n=55 f=4 % (2)	16	89	<LOQ	<LOQ	
	2017	n=14 f=14 % (2)	16	32	<LOQ	<LOQ	
Metalaxyl	2016	n=55 f=11 % (6)	6	29	<LOQ	<LOQ	
	2017	n=14 f=14 % (2)	7	9	<LOQ	<LOQ	
Metazachlor	2016	n=55 f=25 % (14)	5	995	13	180	4
	2017	n=14 f=7 % (1)		21	<LOQ	<LOQ	
Methiocarb	2016	n=55 f=4 % (2)	5	9	<LOQ	<LOQ	
Methomyl	2016	n=55 f=2 % (1)		115	<LOQ	<LOQ	1
Metolachlor	2016	n=55 f=2 % (1)		25	<LOQ	<LOQ	
Propiconazole	2016	n=55 f=62 % (34)	5	246	6	13	2
	2017	n=14 f=79 % (11)	6	150	6	30	2
Prosulfocarb	2016	n=55 f=15 % (8)	5	48	<LOQ	5	
	2017	n=14 f=21 % (3)	5	7	<LOQ	<LOQ	
Simazine	2016	n=55 f=9 % (5)	6	103	<LOQ	5	1
	2017	n=14 f=14 % (2)	6	11	<LOQ	<LOQ	
Tebuconazole	2016	n=55 f=22 % (12)	5	25	<LOQ	<LOQ	
	2017	n=14 f=36 % (5)	5	22	<LOQ	5	
Terbuthylazine-desethyl	2017	n=14 f=14 % (2)	5	6	<LOQ	<LOQ	

Terbutryn	2016	n=55	f=85 %	(47)	5	84	10	12	
	2017	n=14	f=79 %	(11)	5	25	9	10	

Table S7. Concentrations of pesticides (ng/L) found in the groundwater of Llobregat River and Besòs River into the area of study during 2016-2017. Sampling points are shown in Figure 1. No data for a certain year or compound means that for that year the compound was not found or present below limit of quantification when it was analyzed. For the compound list of the method, see Table S1. When for a certain compound and year only one positive is found, the Mean is the concentration value for that compound. For the calculation of the medians, concentrations below LOQ were defined as 1/2 LOQ.

Sampling point	GW-LLO-1						
		samples (n) frequency (f %)	Concentration (ng/L) in positive samples				Cases
	year	(positives)	Min	Max	Median	Average	>100 ng/L
Atrazine-desisopropyl	2016	n=14 f=79 % (11)	31	45	38	33	
	2017	n=10 f=60 % (6)	27	68	28	31	
Carbendazim	2016	n=14 f=100 % (14)	54	218	85	104	6
	2017	n=10 f=30 % (3)	146	260	<LOQ	72	3
Diuron	2016	n=14 f=86 % (12)	19	53	37	33	
	2017	n=10 f=100 % (10)	15	50	38	34	
Imidacloprid	2016	n=14 f=57 % (8)	5	14	5	6	
	2017	n=10 f=40 % (4)	5	10	<LOQ	<LOQ	
Isoproturon	2017	n=10 f=11 % (1)		5	<LOQ	<LOQ	
Propiconazole	2016	n=14 f=7 % (1)		5	<LOQ	<LOQ	
	2017	n=10 f=40 % (4)	5	67	<LOQ	10	
Simazine	2016	n=14 f=43 % (6)	5	6	<LOQ	<LOQ	
	2017	n=10 f=100 % (10)	5	8	6	6	
2-hydroxyterbuthylazine	2016	n=14 f=14 % (2)	26	44	<LOQ	<LOQ	
Terbuthylazine-desethyl	2017	n=10 f=10 % (1)		5	<LOQ	<LOQ	
Terbutryn	2016	n=14 f=29 % (4)	8	9	<LOQ	<LOQ	
	2017	n=10 f=30 % (3)	5	10	<LOQ	<LOQ	

Sampling point	GW-LLO-2						
		samples (n) frequency (f %)	Concentration (ng/L) in positive samples				Cases
	year	(positives)	Min	Max	Median	Average	>100 ng/L
Carbendazim	2016	n=26 f=23 % (6)	87	426	<LOQ	47	3
	2017	n=25 f=4 % (1)		82	<LOQ	<LOQ	
Chlorotoluron	2016	n=26 f=15 % (4)	5	51	<LOQ	5	
	2017	n=25 f=4 % (1)		5	<LOQ	<LOQ	
DEET	2016	n=26 f=8 % (2)		43	<LOQ	<LOQ	
Diuron	2016	n=26 f=23 % (6)	29	333	8	36	3
	2017	n=25 f=48 % (12)	18	45	8	18	
Fenuron	2016	n=26 f=4 % (1)		40	<LOQ	<LOQ	
	2017	n=25 f=4 % (1)		70	<LOQ	<LOQ	
Imidacloprid	2016	n=26 f=8 % (2)	5	16	<LOQ	<LOQ	
Propiconazole	2016	n=26 f=12 % (3)	33	100	<LOQ	9	1
	2017	n=25 f=8 % (2)	6	14	<LOQ	<LOQ	
Simazine	2016	n=26 f=19 % (5)	5	6	<LOQ	<LOQ	
	2017	n=25 f=48 % (12)	5	9	<LOQ	<LOQ	
Tebuconazole	2016	n=26 f=12 % (3)	29	110	<LOQ	9	1
Terbuthylazine	2016	n=26 f=12 % (3)	5	6	<LOQ	<LOQ	
Desethylterbuthylazine	2016	n=26 f=12 % (3)	5	8	<LOQ	<LOQ	
	2017	n=25 f=24 % (6)	5	6	<LOQ	<LOQ	
Terbutryn	2016	n=26 f=19 % (5)	13	37	<LOQ	6	
	2017	n=25 f=44 % (11)	5	16	<LOQ	5	

Sampling point	GW-BES-1

	year	samples (n) frequency (f %) (positives)	Concentration (ng/L) in positive samples				Cases >100 ng/L
			Min	Max	Median	Average	
Atrazine	2016	n=3 f=100 % (3)	18	27	26	24	
	2017	n=4 f=50 % (2)	16	16	9	9	
Bentazone	2016	n=3 f=100 % (3)	34	54	47	45	
	2017	n=4 f=25 % (1)		37	<LOQ	11	
Carbendazim	2016	n=3 f=100 % (3)	101	111	101	104	3
	2017	n=4 f=50 % (2)	120	126	66	68	2
Chlorotoluron	2016	n=3 f=100 % (3)	129	145	131	135	3
	2017	n=4 f=100 % (4)	42	103	72	72	1
Diuron	2016	n=3 f=100 % (3)	27	29	28	28	
	2017	n=4 f=75 % (3)	22	25	23	18	
Fenuron	2016	n=3 f=33 % (1)		38	<LOQ	21	
Imidacloprid	2016	n=3 f=100 % (3)	23	25	24	24	
	2017	n=4 f=75 % (3)	7	27	10	12	
Isoproturon	2016	n=3 f=100 % (3)	27	45	27	33	
	2017	n=4 f=50 % (2)	40	48	21	23	
Metolachlor	2016	n=3 f=33 % (1)		21	<LOQ	<LOQ	
	2017	n=4 f=50 % (2)	15	25	<LOQ	<LOQ	
Metolachlor-ESA	2016	n=3 f=100 % (3)	25	28	25	26	
	2017	n=4 f=25 % (1)		30	<LOQ	<LOQ	
Metribuzin	2017	n=4 f=50 % (2)	12	16	7	8	
Simazine	2016	n=3 f=100 % (3)	24	24	24	24	
	2017	n=4 f=100 % (4)	5	20	13	13	
Tebuconazole	2016	n=3 f=33 % (1)		5	5	5	
	2017	n=4 f=50 % (2)	6	7	<LOQ	5	
Terbuthylazine	2016	n=3 f=100 % (3)	44	50	49	48	
	2017	n=4 f=50 % (2)	31	32	17	17	
2-hydroxyterbuthylazine	2016	n=3 f=33 % (1)		31	<LOQ	<LOQ	
Desethylterbuthylazine	2016	n=3 f=100 % (3)	13	15	15	14	
	2017	n=4 f=75 % (3)	8	11	10	8	
Terbutryn	2016	n=3 f=100 % (3)	7	9	8	8	
	2017	n=4 f=50 % (2)	8	9	5	6	

Table S8. Concentrations of pesticides (ng/L) found in the Barcelona Metropolitan area during 2016-2017. Sampling areas are shown in Figure 1. No data for a certain year or compound means that for that year the compound was not found or present below limit of quantification when it was analyzed. For the compound list of the method, see Table S1. When for a certain compound and year only one positive is found, the Mean is the concentration value for that compound. For the calculation of the medians, concentrations below LOQ were defined as 1/2 LOQ.

Supply Zone	Zone A					
		samples (n) frequency (f %)	Concentration (ng/L) in positive samples			
	year	(positives)	Min	Max	Median	Average
Acetamiprid	2017	n=46 f=2 % (1)		7	5	5
Azoxystrobin	2017	n=46 f=7 % (3)	7	12	5	5
Carbendazim	2017	n=46 f=2 % (1)		31	5	6
DEET	2016	n=80 f=1 % (1)		32	13	13
Imidacloprid	2017	n=46 f=2 % (1)		5	5	3
Metazachlor	2016	n=80 f=8 % (6)	5	12	3	3

Supply Zone	Zone B1					
		samples (n) frequency (f %)	Concentration (ng/L) in positive samples			
	year	(positives)	Min	Max	Median	Average
Azoxystrobin	2017	n=26 f=4 % (1)		6	5	5
Fenuron	2016	n=37 f=5 % (2)	32	69	13	15
Propiconazole	2017	n=26 f=4 % (1)		21	5	6

Supply Zone	Zone B2					
		samples (n) frequency (f %)	Concentration (ng/L) in positive samples			
	year	(positives)	Min	Max	Median	Average
Atrazine-desisopropyl	2016	n=11 f=55 % (6)	28	42	28	25
	2017	n=20 f=25 % (5)	27	47	13	19
Diuron	2016	n=11 f=73 % (8)	25	49	30	28
	2017	n=20 f=80 % (16)	15	48	26	27
Imidacloprid	2016	n=11 f=18 % (2)	5	6	3	3
	2017	n=20 f=15 % (3)	5	6	3	3
Propiconazole	2017	n=20 f=10 % (2)	5	67	3	6
Simazine	2016	n=11 f=36 % (4)	5	6	3	4
	2017	n=20 f=25 % (5)	5	9	5	5
Terbuthylazine-desethyl	2017	n=20 f=15 % (3)	5	7	3	3
2-hydroxyterbuthylazine	2016	n=11 f=27 % (3)	25	50	13	18
	2017	n=11 f=27 % (3)		48	13	14

Supply Zone	Zone C1					
		samples (n) frequency (f %)	Concentration (ng/L) in positive samples			
	year	(positives)	Min	Max	Median	Average
DEET	2016	n=27 f=4 % (1)		27	13	13
Fenuron	2016	n=27 f=7 % (2)	31	63	13	15

Supply Zone	Zone C2		
		samples (n) frequency (f %)	Concentration (ng/L) in positive samples

	year	(positives)	Min	Max	Median	Average
	2016	n=2				
	2017	n=5				

Supply Zone	Zone D					
		samples (n) frequency (f %)	Concentration (ng/L) in positive samples			
	year	(positives)	Min	Max	Median	Average
Azoxystrobin	2017	n=38 f=3 % (1)		8	3	3
Fenuron	2016	n=55 f=2 % (1)		76	13	14
Terbuthylazine	2016	n=55 f=4 % (2)	5	5	3	3

Supply Zone	Zone E					
		samples (n) frequency (f %)	Concentration (ng/L) in positive samples			
	year	(positives)	Min	Max	Median	Average
Azoxystrobin	2017	n=46 f=2 % (1)		5	3	3
DEET	2016	n=76 f=1 % (1)		26	13	13
	2017	n=46 f=2 % (1)		29	13	13
Fenuron	2016	n=76 f=5 % (4)	29	71	13	14
Terbuthylazine	2016	n=76 f=13 % (10)	5	5	3	3
Imidacloprid	2017	n=46 f=2 % (1)		51	3	4
Metolachlor-ESA	2017	n=46 f=2 % (1)		7	3	3

Table S9. Concentrations of pesticides (ng/L) in the DWTP1 during 2016-2017 period. Samples were collected in all stages of treatment observing the hidraulic retention times along the process. Sampling points are shown in Figure 1. No data for a certain year or compound means that for that year the compound was not found or present below limit of quantification when it was analyzed. For the compound list of the method, see Table S1. When for a certain compound and year only one positive is found, the Mean is the concentration value for that compound. For the calculation of the medians, concentrations below LOQ were defined as 1/2 LOQ.

Sampling point	Surface water						
	year	samples (n) frequency (f %) (positives)	Concentration (ng/L) in positive samples				Cases >100 ng/L
			Min	Max	Median	Mean	
2,4-D	2016	n=4 f=25 % (1)		15	<LOQ	<LOQ	
Bentazone	2016	n=4 f=25 % (1)		9	<LOQ	<LOQ	
Carbendazim	2016	n=4 f=100 % (4)	56	109	79	70	2
	2017	n=1 f=100 % (1)		126			1
DEET	2016	n=4 f=25 % (1)		40	13	19	
Diazinon	2016	n=4 f=25 % (1)		6	<LOQ	<LOQ	
Dimethoate	2016	n=4 f=25 % (1)		13	13	13	
Diuron	2016	n=4 f=25 % (1)		20	8	11	
Imidacloprid	2016	n=4 f=100 % (4)	8	13	11	11	
Isoproturon	2016	n=4 f=25 % (1)		12			
Metalaxyl	2016	n=4 f=25 % (1)		14			
Metazachlor	2016	n=4 f=75 % (3)	5	11	5	6	
Propiconazole	2016	n=4 f=25 % (1)		5			
Prosulfocarb	2016	n=4 f=25 % (1)		31			
	2017	n=1 f=100 % (1)		7			
Tebuconazole	2016	n=4 f=25 % (1)		8			
Terbutryn	2016	n=4 f=50 % (2)	6	6	<LOQ	<LOQ	

Sampling point	Sand filter						
	year	samples (n) frequency (f %) (positives)	Concentration (ng/L) in positive samples				Cases >100 ng/L
			Min	Max	Median	Average	
2,4-D	2016	n=3 f=33 % (1)		17			
Bentazone	2016	n=3 f=33 % (1)		7			
Carbendazim	2016	n=3 f=100 % (3)	80	182	90	117	1
DEET	2016	n=3 f=33 % (1)		29			
Diazinon	2016	n=3 f=67 % (2)	5	6	5	5	
Diuron	2016	n=3 f=33 % (1)		15			
Imidacloprid	2016	n=3 f=100 % (3)	9	13	10	13	
Isoproturon	2016	n=3 f=33 % (1)		10			
Metazachlor	2016	n=3 f=67 % (2)	5	6	5	5	
Prosulfocarb	2016	n=3 f=33 % (1)		21			
Terbutryn	2016	n=3 f=67 % (2)	6	7	6	5	
Any compound detected	2017	n=1					

Sampling point	Groundwater						
	year	samples (n) frequency (f %) (positives)	Concentration (ng/L) in positive samples				Cases
			Min	Max	Median	Average	
Diuron	2016	n=1 f=100 % (1)		21			>100 ng/L
	2017	n=1 f=100 % (1)		20			
Simazine	2016	n=1 f=100 % (1)		5			
Terbutryn	2016	n=1 f=100 % (1)		7			

	2017	n=1 f=100 % (1)		8			

Sampling point	Ozone treatment						
	year	samples (n) frequency (f %) (positives)	Concentration (ng/L) in positive samples				Cases >100 ng/L
			Min	Max	Median	Average	
Carbendazim	2016	n=3 f=100 % (3)	35	41	35	37	
	2017	n=1 f=100 % (1)		84			
Fenuron	2016	n=3 f=33 % (1)		29			
Imidacloprid	2016	n=3 f=67 % (2)	5	13	5	7	
Isoproturon	2016	n=3 f=33 % (1)		5			
Prosulfocarb	2016	n=3 f=33 % (1)		17			
	2017	n=1 f=100 % (1)		5			

Sampling point	GAC filtering						
	year	samples (n) frequency (f %) (positives)	Concentration (ng/L) in positive samples				Cases >100 ng/L
			Min	Max	Median	Average	
Carbendazim	2016	n=4 f=25 % (1)		65			
Imidacloprid	2016	n=4 f=25 % (1)		8			
Metazachlor	2016	n=4 f=25 % (1)		5			
Prosulfocarb	2016	n=4 f=25 % (1)		5			
Terbutryn	2016	n=4 f=25 % (1)		9			
Any compound detected	2017	n=1					

Sampling point	Reverse osmosis	
Any compound detected	2016	n=4
Any compound detected	2017	n=1

Sampling point	Blending chamber	
Any compound detected	2016	n=4
Any compound detected	2017	n=1

Sampling point	Finished water	
Any compound detected	2016	n=4
Any compound detected	2017	n=1

Table S10. Concentrations of pesticides (ng/L) in the DWTP4. One single sample was collected along the stages of treatment observing the hidraulic retention times along the process. Sampling points are shown in Figure 1. No data for a certain year or compound means that for that year the compound was not found or present below limit of quantification when it was analyzed. For the compound list of the method, see Table S1.

	DWTP-4		
compounds	raw water (groundwater from GW-LLO-1)	stripping treatment	final chlorination
2-hydroxyterbuthylazine	20	21	21
Carbendazim	46	45	<LOQ
Desisopropylatrazine	48	44	46
Diuron	25	26	20
Imidacloprid	6	6	6

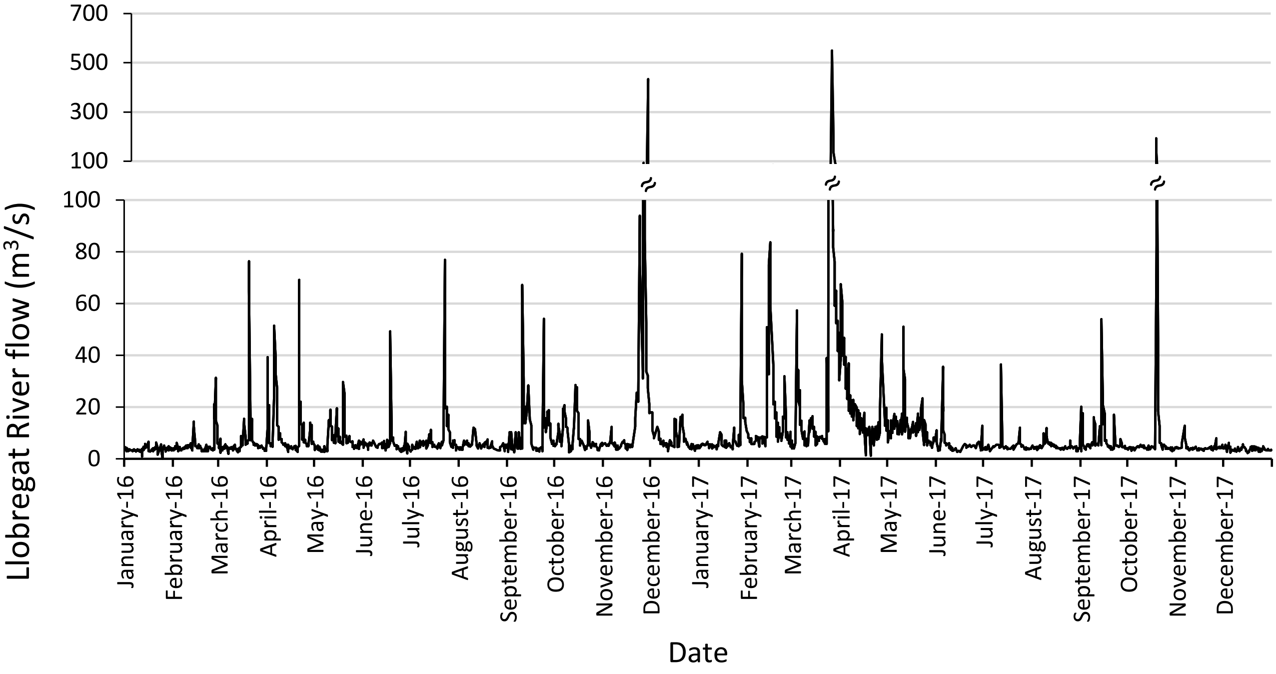

Figure S1. Daily flow (m^3/second) of Llobregat River at the intake of DWTP1 (sampling point LLO-4) during years 2016 and 2017.

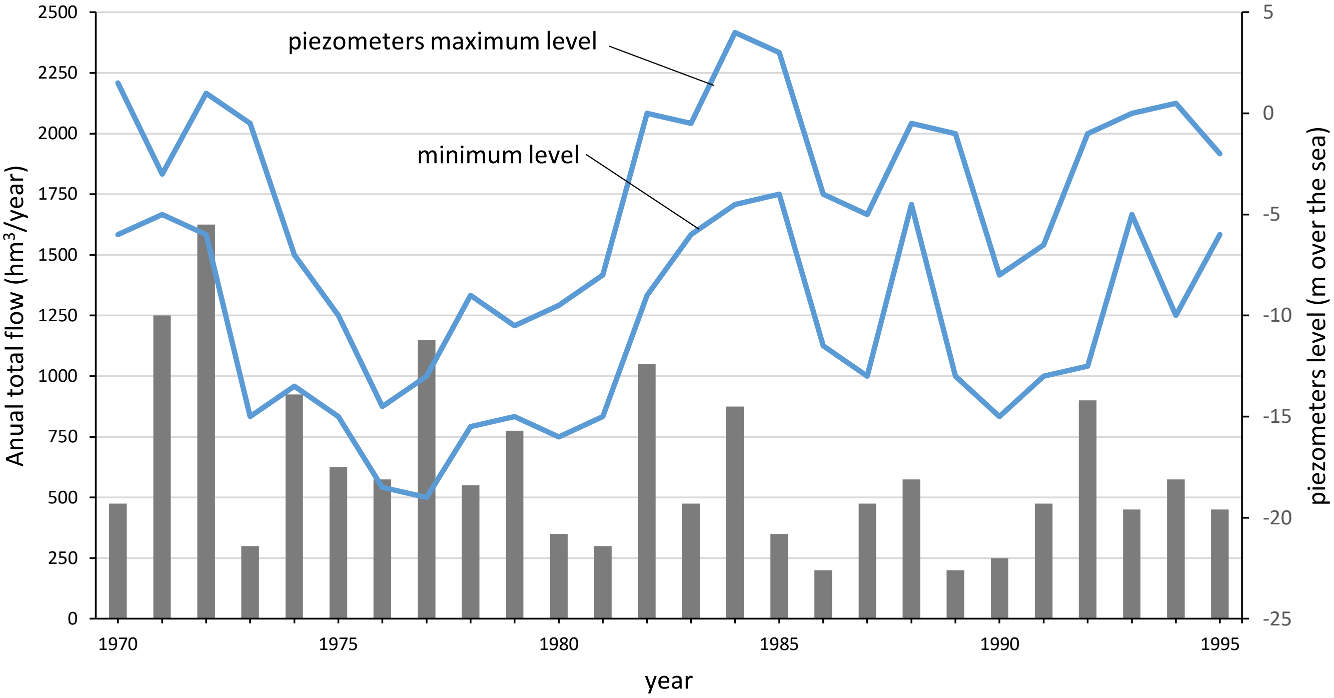

Figure S2. Graphical relationship between yearly accumulated flow (hm^3/year) of Llobregat River at the intake of DWTP1 (sampling point LLO-4) and the piezometers level (maximum and minimum level) of wells associated with drinking water production at DWTP1 (sampling point GW-LLO-2) during years 1970-1995. Chart courtesy of Mr. Jordi Martín Alonso (internal and unpublished data).

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