

CONCORSO PUBBLICO, PER ESAMI, A N. 1 POSTO DI CATEGORIA D POSIZIONE ECONOMICA D1, AREA TECNICA, TECNICO-SCIENTIFICA ED ELABORAZIONE DATI, PER LE ESIGENZE DEL DIPARTIMENTO DI SANITA' PUBBLICA DELL'UNIVERSITÀ DEGLI STUDI DI NAPOLI FEDERICO II (COD. RIF. 2003) INDETTO CON DECRETO DEL DIRETTORE GENERALE N. 436 DEL 30.06.2020 E PUBBLICATO SULLA G.U. IV SERIE SPECIALE – CONCORSI ED ESAMI – N. 53 DEL 10.07.2020

ELENCO DEI QUESITI SORTEGGIATI DAI CANDIDATI

PROVA ORALE DEL 29.09.2020

- 1) Il D.Lgs. 31/2001.
- 2) Impatto sulla salute degli inquinanti ambientali.
- 3) La valutazione degli inquinanti: principali metodologie.
- 4) Spettrofotometria in assorbimento atomico, Principali tecniche di sequenziamento genico e Presentazione in Power Point.

Besòs River, a third river close to Barcelona (18 km long and annual average flow of 4 m³/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 due to 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). drinking water treatment plants 5 can produce 0.5 m³/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 drinking water treatment plants 2.

- 1) Attualità e prospettive del D.Lgs. 31/2001.
- 2) Parametri per il controllo delle acque potabili.
- 3) Metodi per la valutazione degli inquinanti.
- 4) Cromatografia ionica, Elettroforesi e Presentazione in Power Point.

On the other hand, polar and persistent metabolites or transformation products of commercial ingredients are also present in the aquatic environment (Jurado et al., 2012; Postigo et al., 2010). Their presence at the catchment points of drinking water treatment plants (DWTPs) lays out a challenge, because their hydrophilicity makes their removal difficult, even for the most advanced treatments. In fact, the occurrence of some relevant metabolites led to the restriction in the use of certain pesticides in Europe (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).

- 1) Criticità dell'attuale legislazione sulle acque destinate al consumo umano.
- 2) Impatto sulla salute degli inquinanti ambientali.
- 3) Metodi di prelievi di matrici ambientali per la valutazione degli inquinanti.
- 4) Analisi colorimetriche degli inquinanti ambientali, Principali tecniche di sequenziamento genico ed Elaborazione dati in Excel.

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.

- 1) Attuazione della direttiva 98/83/CE: attuali prospettive.
- 2) Descrizione dei parametri organolettici per il controllo delle acque potabili.
- 3) La valutazione degli inquinanti attraverso i metodi di prelievi di matrici ambientali.
- 4) Spettrofotometria in assorbimento atomico, Messa a punto di una tecnica di sequenziamento genico e Archiviazione dati in office.

An on-line sample extraction (0.75 mL) coupled to fast UHPLC-MS/MS method was developed. Good linearity ($r^2 > 0.995$, with less residuals than 15%), accuracies and precisions under 25%, and acceptable expanded uncertainties were obtained for most of the monitored compounds, according to ISO/IEC 17025, obtaining limits of quantification between 5 and 25 ng/L for all compounds. A monitoring campaign on natural and treated waters in the Barcelona metropolitan area was carried out during 2016–2017.

- 1) Acque destinate al consumo umano.
- 2) Metodi di prelievi di matrici ambientali.

- 3) Ricerca di inquinanti in matrici ambientali.

- 4) Cromatografia liquida, PCR e Archiviazione dati con Excel.

Pesticides are probably some of the most studied and monitored chemicals in water resources, not only for environmental reasons, but also because their potential to contaminate drinking water supplies. Carbamates, organophosphorus compounds, pyrethroids, sulfonylureas or triazines are the most important groups. Although the production and use of some of the oldest pesticides have been prohibited or restricted since toxicological data has proved their threat for biota or human health, new compounds less persistent and theoretically safer, such as neonicotinoids (Starnes and Goh, 2012) or azoles (Kahle et al., 2008), have been continuously launched to the market. The number of authorised active ingredients in pesticide formulations is still high (460 in 2016) (EU, 2016), and the pesticides sales market does not stop increasing in Europe, particularly in Spain (Eurostat, 2015).

- 1) Innovazioni apportate dall'attuale legislazione sulle acque destinate al consumo umano.

- 2) Metodi analitici per il controllo delle acque destinate al consumo umano.

- 3) La valutazione degli inquinanti attraverso i metodi di prelievi di matrici ambientali.

- 4) Spettrofotometria in assorbimento atomico, PCR e Presentazione in Power Point.

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 years 2016 and 2017 to intensively sample the Llobregat River basin, its tributaries and its groundwater aquifer, other metropolitan sources used to produce drinking water, as well as the distribution water system in all water supply zones according to the European Drinking Water Directive. In addition, the method allowed the evaluation of the effectiveness of removal of these chemicals in different drinking water treatment plants involved in drinking water served to almost 3 million consumers daily.

- 1) Attuazione della direttiva 98/83/CE: principali sviluppi.

- 2) I parametri per la rilevazione della potabilità delle acque.
- 3) La valutazione degli inquinanti attraverso i metodi di prelievi di matrici ambientali.
- 4) La spettrometria di massa a plasma accoppiato induttivamente (ICP-MS), Definizione ed utilizzo della PCR e Utilizzo di Word.

The quality of water intended for human consumption is regulated under the Drinking Water Directive (EU 2015/1787). Unlike USA Safe Drinking Water Act, where limits are set according to toxicological data, the European directive relies on the precautionary principle, and it only establishes a general maximum individual concentration of 0.1 µg/L for the most relevant pesticides. Periodic controls in the distribution network, intermediate deposits and the outflow of treatment plants are defined. The main weakness of this model is the time gap between sampling and obtaining the analytical results necessary to make decisions, since the water supply does not stop meanwhile. For this reason, the Water Safety Plans proposed by the World Health Organization in 2004 (WHO, 2004) shifted the focus from the final product control to the implementation of preventive risk management and critical points analysis to consistently ensure the safety of final drinking water.

- 1) Attuali disposizioni legislative adottate nel settore delle acque destinate al consumo umano.
- 2) Descrizione dei parametri microbiologici per il controllo delle acque potabili.
- 3) Effetti sulla salute degli inquinanti ambientali.
- 4) Cromatografia ionica, Definizione di Sequenziamento genico ed Archiviazione dati in office.

The aim of this work is to find adequate water treatments to produce save water at water treatment plants for drinking purposes, despite the fact that contaminants are every day higher and more varied in our rivers. With this intention, an analytical multi-residue method was developed for >96 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), some pesticides from a list of European monitoring programs and some selected transformation products.

- 1) Criticità e innovazioni apportate dal D.Lgs. 31/2001.
- 2) Parametri per il controllo delle acque potabili.
- 3) Ricerca di inquinanti in matrici ambientali.
- 4) Cromatografia liquida, Amplificazione nel sequenziamento genico e Presentazione in Power Point.

Sampling points are described in Fig. 1 for natural waters, and in Fig. 3 for drinking waters. For natural waters the prefix LLO-, CA-, AN-, RU- and BE- were used for sampling points at Llobregat River, Cardener River, Anoia River, Rubí Creek and Besòs River, respectively. Incremental numbers were used along the rivers from the upper to the lower stretch. The prefix GW- was used for groundwaters. For drinking waters each sampling point correlates with the supply area name. Samples were collected by a trained team during years 2016–2017 following an accredited procedure based on ISO 5667-5:2006

- 1) Legislazione sulle acque destinate al consumo umano: ambiti applicativi.
- 2) Descrizione dei parametri organolettici per il controllo delle acque potabili.
- 3) Metodi utilizzati per la ricerca di inquinanti in matrici ambientali.
- 4) Cromatografia liquida, Fasi del sequenziamento genico e Software applicativi.

Water safety plans, adapted to the real needs of each supply, require the identification of all potential hazards in all the stages from catchment to consumption to calculate the risks and to adopt the right preventive measures. Such identification must be based on reliable analytical evidence and historical data. In this sense, monitoring of pesticides means a special challenge, due to the high number of existing compounds and the variability of periods of use. The number of monitored compounds is usually limited, and compounds are selected according to sanitary standards, previous monitoring programs as well as analytical feasibility. Recent studies disclosed that analysis of non-previously reported compounds can appreciably change the risk assessment associated to sampling campaigns (Moschet et al., 2014; Reemtsma et al., 2013; Schreiner et al., 2016). For this reason, monitoring programs previous to risk assessment should be as complete as possible and take into account the characteristics of the geographical area (market sales, typology of agriculture and industry, population and wastewater management).

- 1) La legislazione sulle acque destinate al consumo umano.
- 2) Metodi analitici per la ricerca di inquinanti in matrici ambientali.
- 3) Metodi di prelievi di matrici ambientali per la valutazione degli inquinanti ambientali.
- 4) Cromatografia liquida, Principali tecniche di sequenziamento genico e Software applicativi.

The distribution net of drinking water is composed by 4500 km of pipelines, 72 reservoirs and 8 different sources of water distributed in seven water supply zones. 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.

- 1) Attualità e prospettive del D.Lgs. 31/2001.
- 2) Descrizione dei parametri organolettici e microbiologici per il controllo delle acque potabili.
- 3) Ricerca di inquinanti in matrici ambientali.
- 4) Analisi colorimetriche degli inquinanti ambientali, Amplificazione nel sequenziamento genico e Presentazione in Power Point.

Results showed that pesticide contamination at the low stretch of Llobregat River and in its aquifer is severe. The maximum concentrations were in the range of few $\mu\text{g/L}$ for carbendazim, DEET, diuron and propiconazole, and in the range 0.1–0.5 $\mu\text{g/L}$ for bentazone, imidacloprid, isoproturon, simazine, metazachlor, methomyl, terbutryn and tebuconazole. However, the efficiency of advanced treatments in the drinking water treatment plants involved in drinking water production in the Barcelona metropolitan area allows the complete removal of pesticides and a safe water production for consumers. The method shows a good analytical performance for most compounds with a fast sample preparation and analysis. In addition, it has updated the knowledge about the occurrence of pesticides in the Barcelona city area

- 1) Attualità e prospettive del D.Lgs. 31/2001.
- 2) Descrizione dei parametri chimico-fisici per il controllo delle acque potabili.
- 3) Ricerca di inquinanti in matrici ambientali.
- 4) Cromatografia gassosa, PCR e archiviazione dati con Excel.

The progressive improvement of analytical instrumentation during the last decades helps to fulfil those requirements. In the case of pesticides of concern, which are gradually more hydrophilic, liquid chromatography (LC) coupled to mass spectrometry (MS) has become the best option due to the advance of

ionization techniques (Thurman et al., 2001) and analysers (Alder et al., 2006; Ferrer and Thurman, 2007; Leendert et al., 2015), as well as the progress from high performance LC (HPLC) to ultra-high performance LC (UHPLC) (Marín et al., 2009; Mezcua et al., 2006). However, despite these instrumentation improvements, sample preparation is still usually needed, which increases the potential cost. Also, the total analysis time is a source of error in the analytical method, which sometimes hinders the validation of measurements to meet the growing legislative requirements in terms of precision and accuracy. On-line techniques help to bypass those problems. On-line as Solid Phase extraction (SPE) coupled with LC is nowadays considered an elegant alternative technique for the extraction of pesticides residues from water, as it provides shorter times of analysis, miniaturization and automation, with a consequent improvement of reproducibility, accuracy and sensitivity of the extractive process (Kampioti et al., 2005; Postigo et al., 2010; Singer et al., 2010).

- 1) Attualità e prospettive del D.Lgs. 31/2001.
- 2) Descrizione dei parametri microbiologici per il controllo delle acque potabili.
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- 4) La spettrometria di massa a plasma accoppiato induttivamente (ICP-MS), Elettroforesi ed Elaborazione dati in Excel.

Fig. 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 drinking water treatment plants 1 and drinking water treatment plants 3 and it supplied treated water to the Western part of the Barcelona metropolitan area. Ter River water produced in drinking water treatment plants 2 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 >1% of water is therein produced and water is blended with water that comes from drinking water treatment plants 1 and drinking water treatment plants 3 in R1. Since 2012, a 12 km long pipe is able to transport bidirectionally 4 m³/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 drinking water treatment plants 2 and drinking water treatment plants 3 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

- 1) Il D.Lgs. 31/2001.
- 2) I controlli analitici delle acque destinate al consumo umano.
- 3) Effetti sulla salute degli inquinanti ambientali.

- 4) Cromatografia gassosa, Sequenziamento genico e Software applicativi.

Their presence in the aquatic environment comes from the agricultural activity, as well as urban, industrial and household widespread usages. While pesticides used in the agriculture reach the aquatic environment directly, the main inputs from urban and industrial usages in surface waters are discharges of effluents from wastewater treatment plants (WWTPs), as they are not removed properly in secondary treatments (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 where the water has to be totally or partially reused.

- 1) Acque destinate al consumo umano.
- 2) Parametri per il controllo delle acque potabili.
- 3) Metodi per la valutazione degli inquinanti ambientali.
- 4) La spettrometria di massa a plasma accoppiato induttivamente, Sequenziamento genico e Utilizzo dell'Excel.

Barcelona metropolitan area has a drinking water demand for almost three million inhabitants, although its sources of water are scarce because of its Mediterranean climate. Their main sources (Fig. 1) are the Llobregat River (surface and groundwater) and the Ter River (52% and 24% respectively). Many European rivers have fairly constant flows $>1500 \text{ m}^3/\text{s}$, but Mediterranean rivers are characterized by their low average flows with intermittently high flow peaks, such as Llobregat River ($22 \text{ m}^3/\text{s}$ of annual average flow but with a 2–5 m^3/s flow most of the days of the year, Fig. S1) or Ter River (annual average flow of $27 \text{ m}^3/\text{s}$). In addition to this water scarcity, the management of drinking water in the Mediterranean area has, consequently, some other extra difficulties in comparison 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 like the construction of a desalination sea water treatment plant (SWTP) ($2.3 \text{ m}^3/\text{s}$ maximum from up to 22.5% of Barcelona metropolitan area consumption if needed) which started operating in 2009, or 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

- 1) Acque destinate al consumo umano: attuali disposizioni legislative.
- 2) I controlli analitici delle acque destinate al consumo umano.
- 3) Impatto sulla salute degli inquinanti ambientali.
- 4) Analisi colorimetriche degli inquinanti ambientali, Messa a punto di una tecnica di sequenziamento genico e Archiviazione dati in office.

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.

**Per ordine del Presidente
il Segretario della Commissione
F.to Annamaria Cincinnato**