

DETERMINATION OF PHARMACEUTICAL RESIDUES IN WATERS FROM GRAN CANARIA ISLAND USING A SPE-HPLC-ESI/MS/MS METHOD

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Abstract

A solid phase extraction followed by liquid chromatography–electrospray ionization tandem mass spectrometry (SPE-HPLC-ESI-MS/MS) method was developed for the determination of different pharmaceutical compounds in environmental water matrices. These analytes are widely consumed by the society for different purposes and when they are excreted to the wastewater treatment plants (WWTPs) are not efficiently eliminated. Once there, the compounds can reach environmental waters by several ways, one of them using sewage water for the irrigation. In this work we analyzed the water samples from a hydrogeological basin that may be affected for infiltration process. Six of the seven studied compounds could be determined, carrying out their temporal evolution for one year.

Keywords: pharmaceuticals, water, SPE, HPLC– mass spectrometry

Introduction

Pharmaceutical compounds are widely used and they can reach the WWTPs in very high concentrations, which are unable to remove them completely. Thus, urban wastewaters typically have a strongly contaminating effect on the natural aquatic systems (Martinez et al, 2009). However, their environmental concentrations are very low, for that these analytes need to be extracted and preconcentrated prior to their analysis. In this way, a solid-phase extraction (SPE) step prior to their determination has been very efficient (Moldovan, 2006). In this work we optimise a method that includes SPE followed of liquid chromatography–electrospray ionization tandem mass spectrometry (HPLC-ESI-MS/MS) to the determination of atenolol (B-blocker), metamizol (analgesic), fluoxetine (antidepressant), caffeine (stimulant), and its metabolite paraxanthine, nicotine and permethrin in different environmental water samples. This optimised procedure was applied to different groundwater samples (wells, probes and gallery waters) taken in a hydrogeological basin of Gran Canaria island that may be affected for infiltration process from a golf court irrigated with deperated waters. A preliminary sampling was carried out around of the basin and then five significant samples were selected for a temporal monitoring of the concentrations of pharmaceutical compounds.

Methods

A Varian 320-MS LC/MS/MS system (triple quadrupole) equipped with an electrospray ionisation (ESI) interface was employed for the determination of the compounds. The detection conditions for each compound by direct infusion of pure standard and are shown in Table 1. For the chromatographic separation a Waters Sunfire C18 3.0 × 100 mm (3.5 µm particle size) stationary phase and a mobile phase consisting of methanol and water with 0.2 % (v/v) formic acid and 5 mM ammonium formate were used. The flow-rate was 0.2 mL/min and the sample volume injected was 10 µl under pick-up conditions. The optimum conditions for the solid phase extraction were as follow: cartridge, Oasis HLB; sample volume, 200 mL; sample pH, 8 and flow rate, 10 mL/min. For the elution step 2 mL of methanol at flow rate 1 mL/min was employed.

Table 1. Mass spectrometer parameters for the analytes detection.

Compound	Retention time (min)	Precursor ion (m/z)	Cone (V)	Fragment ions (m/z)
Nicotine	2.0	163.2	30	83.9 (22.5), 79.8 (21.5)
Atenolol	5.0	267.3	56	145 (23.5), 190 (16.5)
Metamizole	7.1	218.1	40	56.1 (12.5), 97 (11.5)
Paraxanthine	9.2	181.2	52	123.9 (17)
Caffeine	11.3	195.1	30	138 (18)
Fluoxetine	17.4	310.3	30	44.1 (6.5), 148 (5.5)
Permethrin	29.1	310.3	36	236.1 (8)

Results and discussion

Once optimised the extraction and the determination procedures the limits of detection (LODs) and quantification (LOQs) were in the range 2.86–39.39 and 9.53–131.30 ng·L⁻¹, respectively. Then, we applied it to the determination of target analytes in the water samples. The sampling was carried out in a hidrogeological basin of the north-east of Gran Canaria island. In the first sampling we analysed sixteen samples including waters from wells, galleries and probes (Fig 1). Between them, we choose the five points where higher concentrations were measured for carry out a monitored every three months during one year.

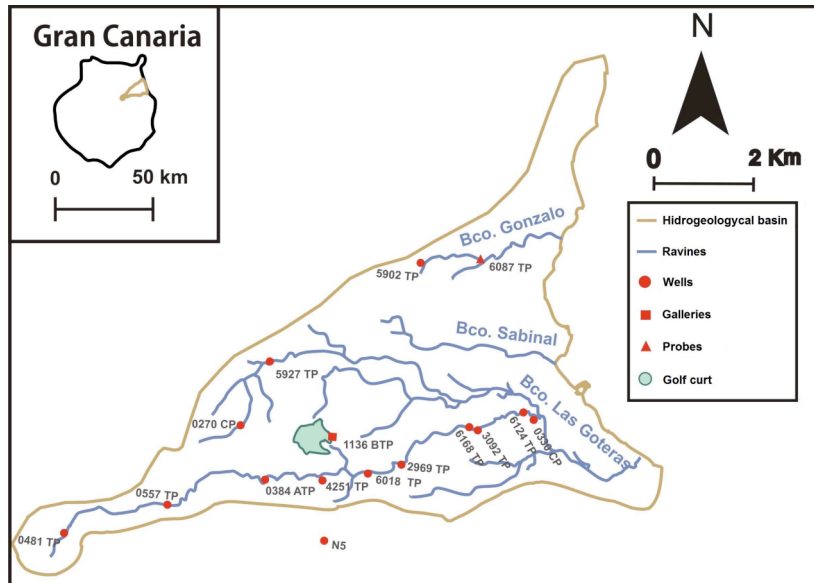


Figure 1. Location of analysed samples.

Fig 2 shows the concentration obtained for each analyte and for each sampling point during a year. Except permethrin, which was not found in any location, all the analytes were detected in some sample. Nicotine and caffeine were detected in almost all samples, presenting high concentrations throughout the year. Atenolol and metamizol were measured in the four sampling, although they were found in a greater number of points in the first of them. On the other hand, metamizol and fluoxetine were measured only in a timely manner.

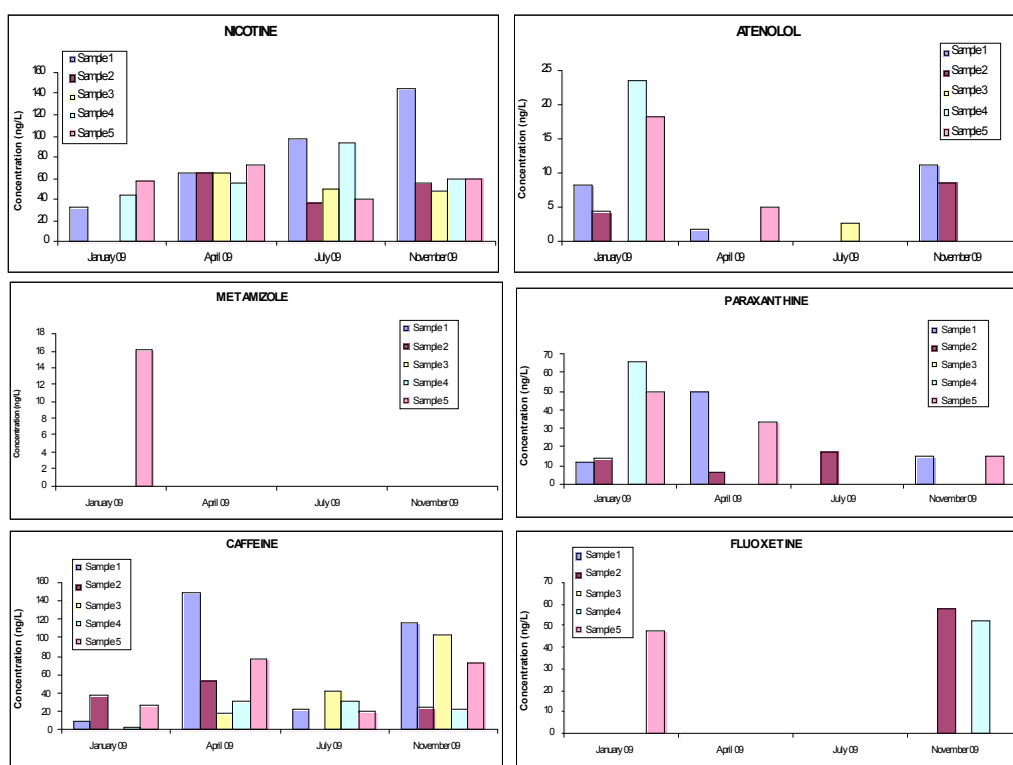


Figure 2. Temporal evolution of analyte concentrations in different samples of gallery and wells

Conclusions

The established solid-phase extraction–liquid chromatography–electrospray ionization tandem mass spectrometry (SPE–HPLC–ESI–MS/MS) procedure allows to determine concentrations of different emerging contaminants in environmental samples in a simple, reliable and rapid manner. We analysed five samples (one of gallery water and four from wells) within of a hidrogeological basin and the sampling was carried out every three months for one year. Almost all the analytes were detected, which demonstrates the need of improve the treatments of sewage waters when these are reused.

References

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