

INTRODUCTION

Determination and control of emerging pollutants have been important topics in environmental analytical chemistry in the last decades. One important group of these contaminants is the hormonal residues, which are considered Endocrine Disrupting Compounds (EDCs). These compounds are defined as chemical substances capable of altering the natural hormonal equilibrium producing harmful effects in animals, humans and their progeny [1]. The consumption of hormones has been increased exponentially in the last decades due to the use of hormones in human and veterinary medicine. Since 1990s some studies established that the main pathway of these compounds to go into the environment is through effluent of wastewater treatment plants (WWTPs). Because of that, many studies in the last years determine the concentrations of sexual hormones in water and wastewater samples [2,3].

In this study, the determination of a group of several natural and synthetic hormones (estrogens, androgens, progestogens and corticosteroids), is presented. For their determination a method based on Solid Phase Extraction (SPE) combined with ultra-high performance liquid chromatography coupled to mass spectrometry detection (UHPLC-MS/MS) have been chosen.

The hormonal compounds have been studied in wastewater samples from four wastewater treatment plants around Gran Canaria island (Spain), with different water treatment methods (WWTP₁ has a membrane bioreactor, WWTP₂ and 4 use activated sludge technology and WWTP₃ uses natural treatment methods) to evaluate the presence of this type of compounds in different settlements of the island.

EXPERIMENTAL PROCEDURE

Chromatographic conditions

Instrument	Waters ACQUITY UPLC with TQ Detector
Column	ACQUITY UHPLC BEH Waters C ₁₈
Injection volume	10 µL
Flow rate	0.3 mL·min ⁻¹
Mobil phases	A: Water (0.1% v/v NH ₃) B: Methanol

Gradient used

Time (min)	% (A)	% (B)
0.00	80	20
1.50	40	60
2.75	25	75
3.75	25	75
6.00	80	20
6.50	80	20

Optimum SPE conditions

Cartridge	SepPak C ₁₈ 6cc (Waters)
Sample volume	250 mL
Sample pH	8
Ionic strength	0% NaCl
Wash step	5 mL Milli-Q water
Desorption solvent	Methanol
Desorption volume	2 mL (1 mL·min ⁻¹)
Cartridge	SepPak C ₁₈ 6cc (Waters)

RESULTS

Analytical parameters

Compound	RT ^a (min)	LOD ^b (ng·L ⁻¹)	RSD ^c (%)		Recovery (%)	
			(25 ng·L ⁻¹) n=6	(150 ng·L ⁻¹) n=6	(25 ng·L ⁻¹) n=3	(150 ng·L ⁻¹) n=3
Estriol	2.12	1.35	5.12	6.50	106.6 ± 8.2	99.0 ± 1.8
Prednisone	2.29	0.27	12.9	4.79	121.3 ± 5.3	105.0 ± 3.3
Cortisone	2.32	0.05	4.55	4.50	118.5 ± 1.2	103.2 ± 6.3
Prednisolone	2.45	0.18	6.90	4.56	112.9 ± 5.6	99.2 ± 3.1
Boldenone	2.87	0.17	5.67	4.47	117.2 ± 3.5	112.7 ± 10.8
Nandrolone	2.93	1.00	3.83	3.81	119.4 ± 4.6	102.2 ± 5.7
Norethisterone	2.95	0.22	7.08	4.37	113.0 ± 1.8	99.3 ± 5.1
17β-estradiol	2.97	1.63	12.4	6.57	120.4 ± 8.5	103.0 ± 7.8
Estrone	2.99	0.35	3.51	4.87	122.2 ± 9.9	109.3 ± 2.5
17α-ethinylestradiol	3.00	2.95	6.84	6.63	--	103.0 ± 10.6
Diethylstilbestrol	3.02	0.16	9.15	5.79	98.8 ± 14.2	80.4 ± 12.0
Testosterone	3.15	0.04	6.33	3.82	118.7 ± 3.3	103.3 ± 5.4
Norgestrel	3.29	0.32	5.14	3.68	114.9 ± 2.5	103.4 ± 4.4
Megestrol acetate	3.54	0.22	8.69	4.98	107.4 ± 1.2	99.4 ± 3.4

^a Retention time ^b Detection limit ^c Relative Standard Deviation

Real samples

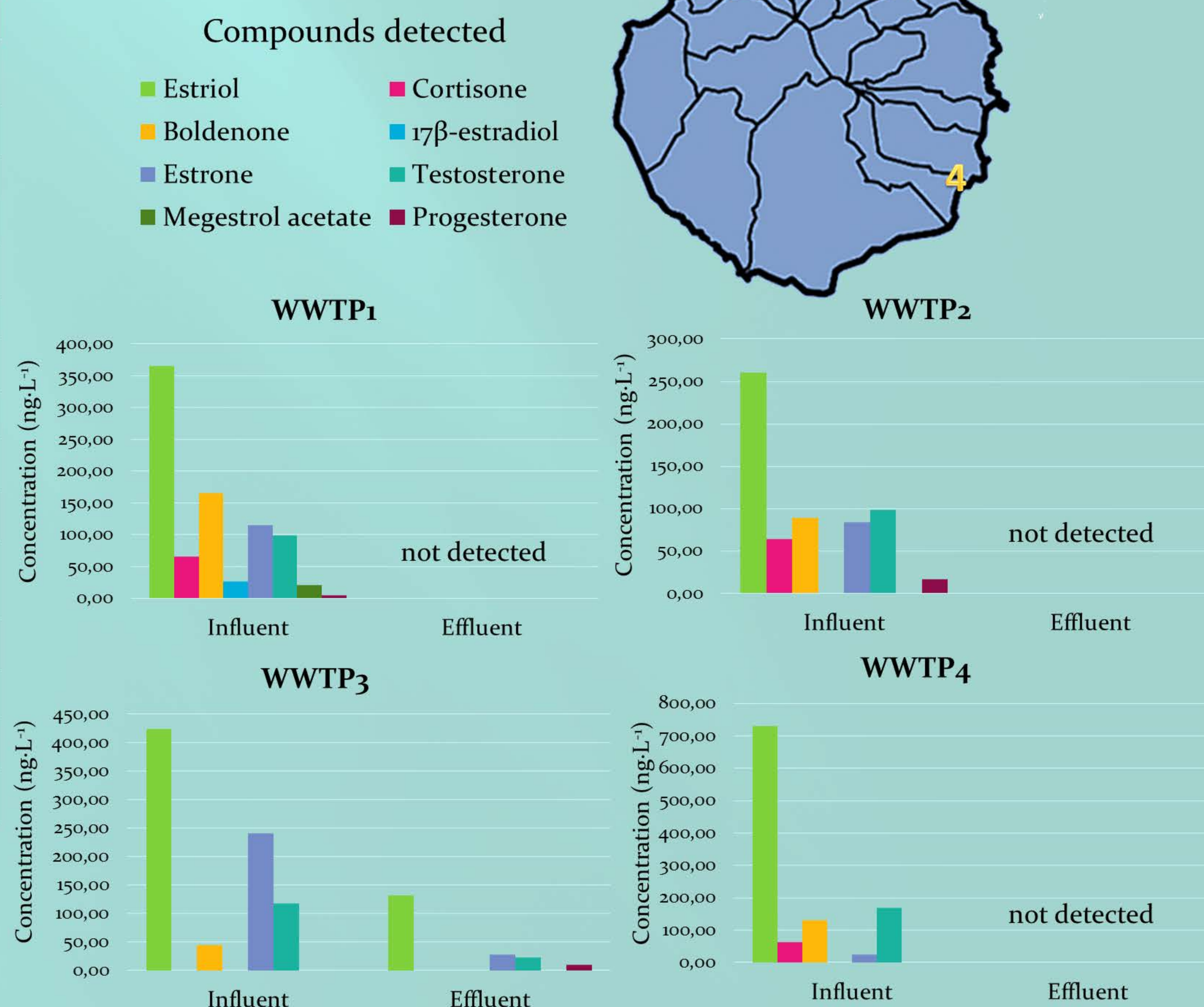


Fig. 2: Concentrations detected (ng·L⁻¹) at different WWTPs

CONCLUSIONS

An analytical method for the simultaneous extraction, preconcentration and determination of fifteen hormones in wastewater matrices has been optimized and developed, obtained high recoveries and RSD lower than 13%. The application of the method to samples from two different WWTPs showed that eight hormones were detected at the different WWTPs, ranging from few ng·L⁻¹ to various cents of ng·L⁻¹. Hormones were detected only in influent samples of three WWTPs, and only in WWTP₃, hormones were detected in influent and effluent samples.

REFERENCES

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