

# Occurrence and removal of hormone residues from a campus wastewater with constructed wetland mesocosms

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## INTRODUCTION:

Steroid hormones are considered as endocrine disruptor compounds and emerging pollutants because they produce changes over aquatic biota<sup>1</sup> as feminization, hermaphroditism and changes of fish behaviour. Conventional and natural wastewater treatment plants (WWTPs) such as constructed wetlands must face the challenge of removing these compounds because the purified waters are reused in different activities. Not only is the layout of the treatment plant important in the design, but also the use of new materials with high sorption capability towards hormones. In this work, both of these critical factors have been studied in constructed wetland mesocosms (CWs) in Gran Canaria (Spain).

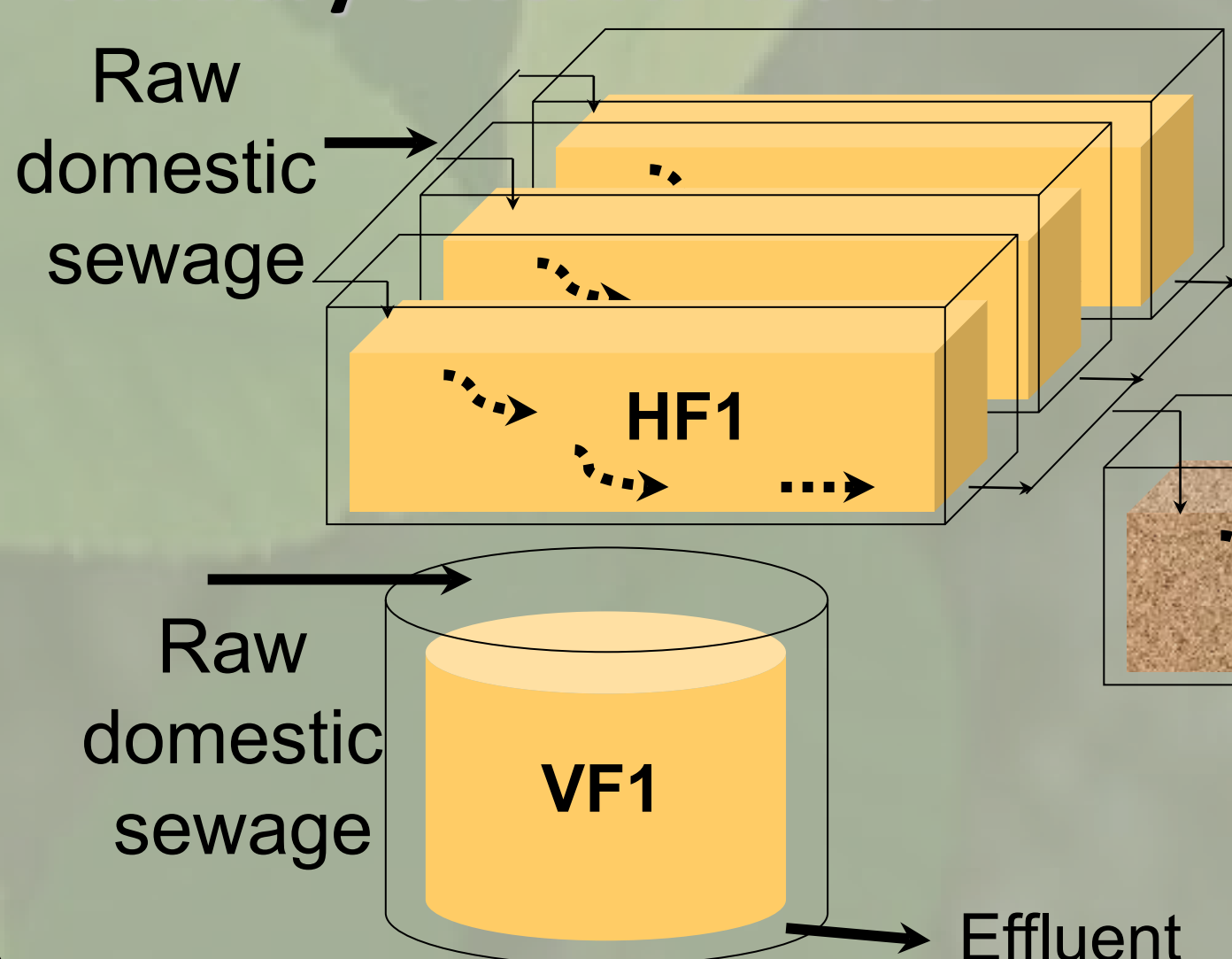
## EXPERIMENTAL:

### Compounds studied:

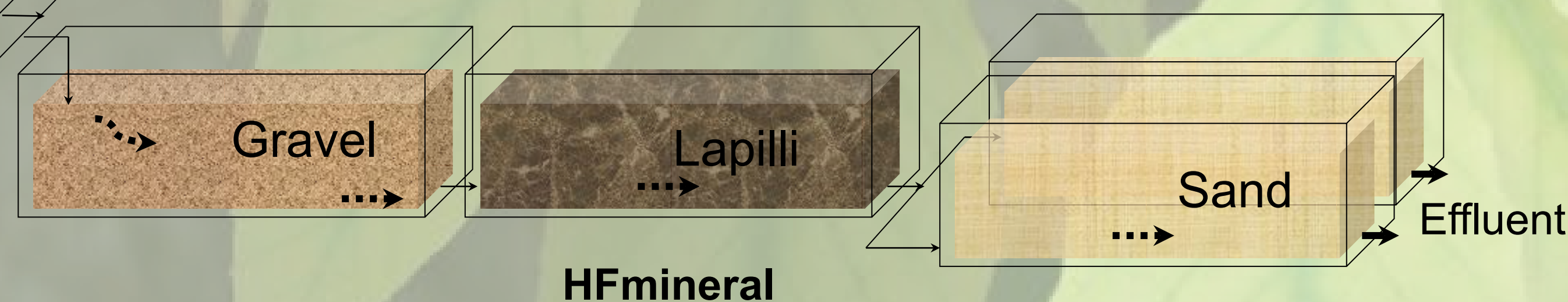
Estrogens	Androgens	Progestogens	Corticosteroids
Diethylstilbestrol (DES)	Boldenone (BOL)	Norethisterone (NOR)	Prednisone (PRD)
17 $\beta$ -estradiol (E2)	Nandrolone (NAN)	Norgestrel (NRG)	Cortisone (COR)
Estrone (E1)	Testosterone (TES)	Megestrol Acetate (MGA)	Prednisolone (PRDL)
Estriol (E3)		Progesterone (PRO)	

### Layout of the CW mesocosms:

#### Primary CWs: HF vs. VF



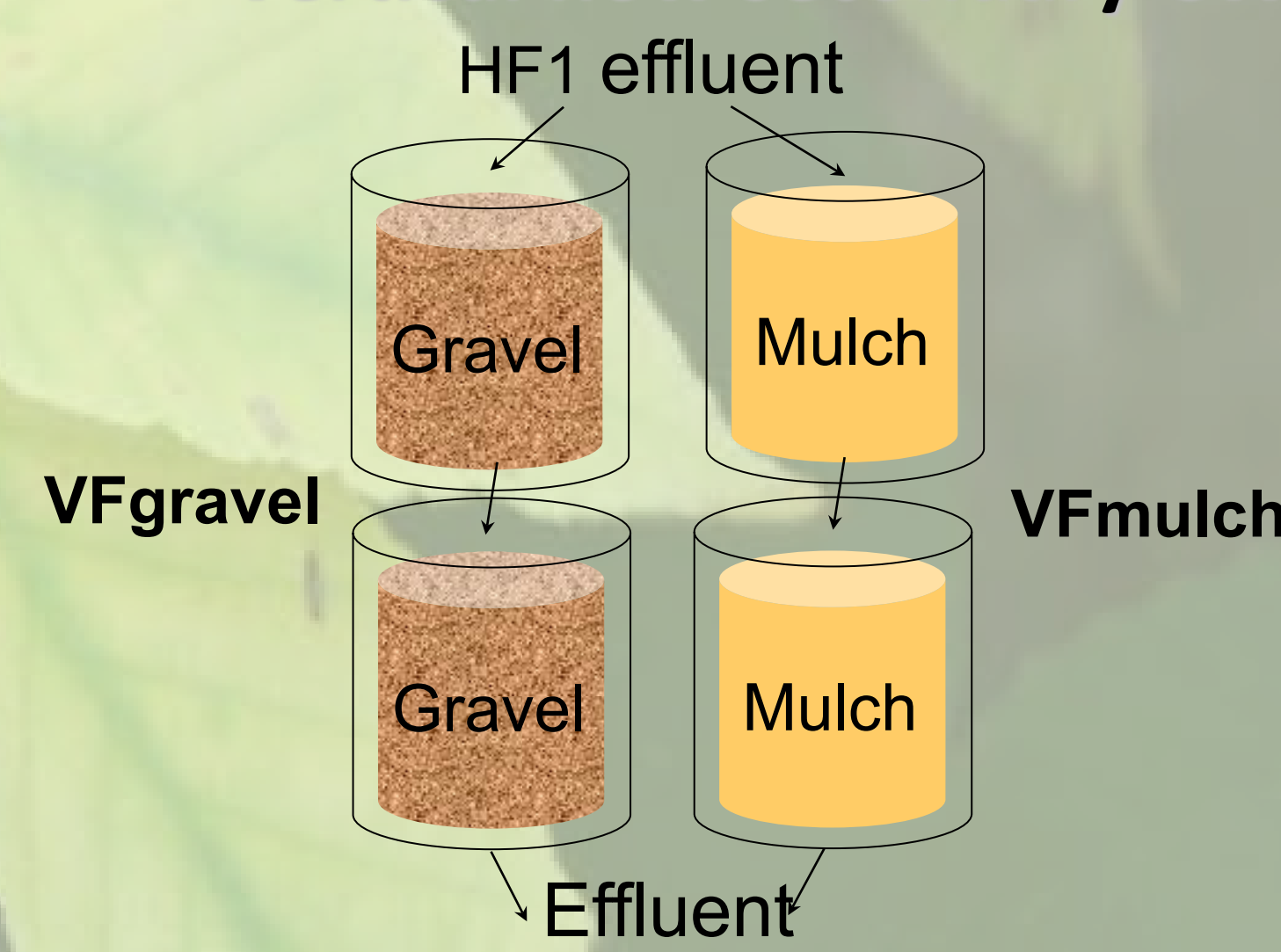
#### Horizontal flow secondary CWs



### Extraction and determination system<sup>2</sup>:

- Extraction system:** on-line SPE.
  - Two Oasis HLB columns (20  $\mu$ m, 2.1x30mm) working in parallel.
  - Flow rate: 2 mL $\cdot$ min<sup>-1</sup>.
- Detection system:** UHPLC-MS/MS (ESI interface)
  - Column: ACQUITY UPLC BEH Waters C18 (50 x 2.1 mm, 1.7  $\mu$ m)
  - Mobile phase: A: Water + 0.1% NH<sub>3</sub>; B: Methanol

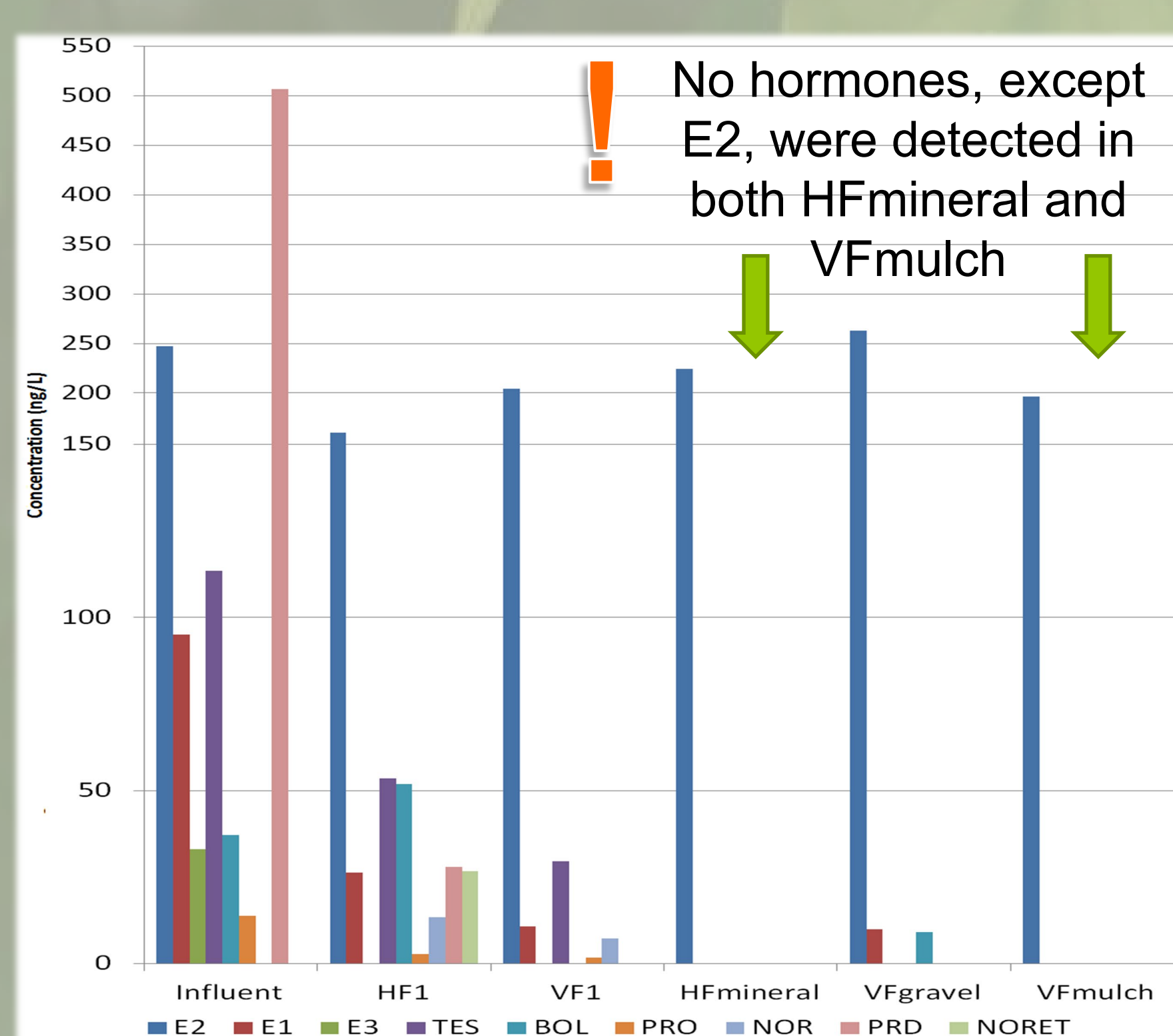
#### Vertical flow secondary CWs



## RESULTS:

### Concentrations of detected hormones in constructed wetland:

Medium values of 8 campaigns. Samples were taken weekly

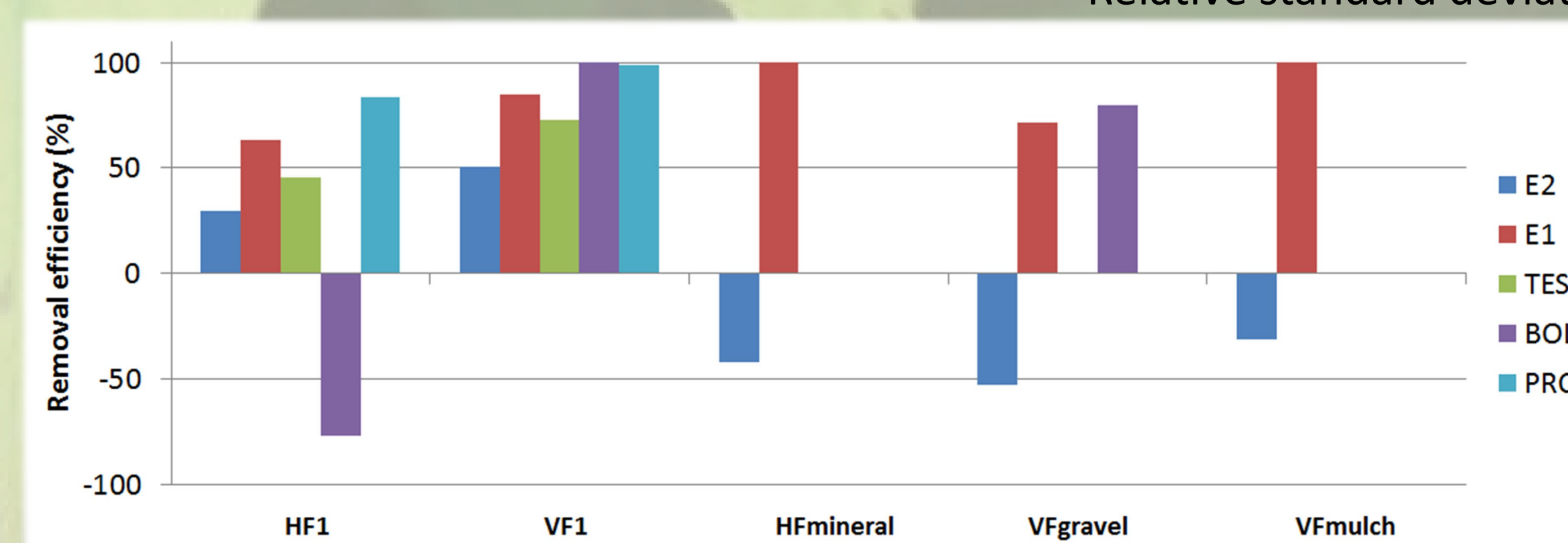


### Analytical parameters:

Compound	Detection limit (ng $\cdot$ L <sup>-1</sup> )	Recovery (%)	RSD* (%)
Estrogens	4.1 – 13.2	42.3 – 104.0	7.3 – 26.4
Androgens	0.7 – 4.1	43.1 – 67.5	3.3 – 9.6
Progestogens	0.5 – 2.3	34.5 – 154.4	2.9 – 11.6
Glucocorticoids	2.1 – 9.2	60.7 – 100.0	3.2 – 11.5

\* Relative standard deviation

### Removal of steroid hormones:



## CONCLUSIONS

Primary vertical flow CW was more efficient than a primary horizontal flow CW in the removal of hormones. Of the secondary CWs tested, the mulch-based, vertical flow CW was the most efficient. It can be concluded that palm mulch is a better substrate than gravel for VFs regarding hormone removal. With the exception of 17 $\beta$ -estradiol, a horizontal subsurface flow combining palm mulch and mineral substrate can also achieve complete hormone removal. The automated online-SPE-UHPLC-MS/MS method used showed a very good reproducibility and little sample handling.

## ACKNOWLEDGEMENTS

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## REFERENCES

- [1] H. Chang, Y. Wan, S. Wu, Z. Fan and J. Hu, Water Res., 2011, 45, 732–740
- [2] R. Guedes-Alonso, Z. Sosa-Ferrera, J. J. Santana-Rodríguez, Anal. Methods, 2015, 7, 5996-6005