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Identification of steroid hormones transformation products in wastewater samples from a combined macrophyte pond-constructed wetland system based in Gran Canaria (Spain) using UHPLC-MS-QToF

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Current monitoring methods cover only a small part of the growing number of contaminants of emerging concern (CECs) that are released into the environment and whose fate remains poorly understood. One class of CECs that has been receiving the attention of the scientific community is steroid hormones due to their persistence and tendency to bioaccumulate. After reaching wastewater treatment plants, these compounds undergo numerous transformations through a variety of poorly understood processes, leading to the creation of transformation products (TPs) that are not well known. The aim of this work was to identify the main TPs of three well-known steroid hormones – testosterone, levonorgestrel and cortisone - along a natural wastewater treatment system, in order to evaluate their presence and potential removal. The water samples, from a combined macrophyte pond-constructed wetland (CW) system based in Tafira (Gran Canaria, Spain), were collected from three sampling points (influent, pond effluent and CW effluent). Using hormone-specific molecularly imprinted polymer cartridges, the samples were subjected to an improved SPE extraction that was more selective than the others available sorbent phases. A UHPLC-MS-QToF was employed for the analysis, which allowed to identify specific TPs using precise m/z ratios of precursor and fragment ions in conjunction with retention times through the use of a "suspect screening" protocol. A number of TPs have been identified, taking testosterone, levonorgestrel and cortisone as starting compounds. Additionally, it was demonstrated that more complex molecules like boldenone, androst-1,4,9(11)-triene-3,17-dione, and 3α -5 β -tetrahydronorgestrel were found in the influent but disappeared in the effluent. Only the effluent included smaller molecules such 9,17-dioxo-1,2,3,4,10,19-hexanorandrostane-5-oic acid. This demonstrated how these contaminants were transformed and partially removed from the wastewater by the pond-CW system.