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Review

# Occurrence and geodatabase mapping of three contaminants of emerging concern in receiving water and at effluent from waste water treatment plants – A first overview of the situation in the Republic of Ireland

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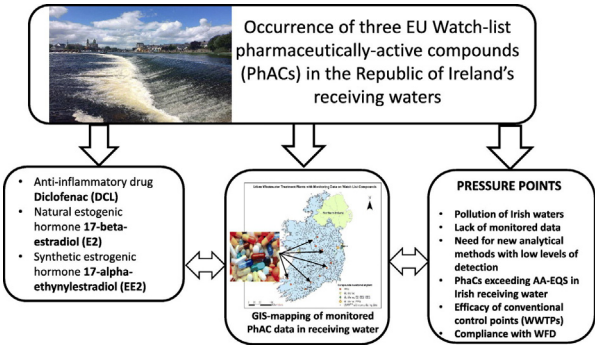
## HIGHLIGHTS

- Occurrence and mapping of 3 EU Watch list substances in Irish aquatic environment
- Lack of monitored data for CECs given number of river basin catchments and control points
- Need for new analytical techniques with low appropriate levels of detection to meet WFD limits
- Control measures frequently do not fully remove these harmful chemicals.
- Mapping of CECs will strategically inform future upgrades to important control points.

## GRAPHICAL ABSTRACT

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## ABSTRACT

This constitutes the first study to address occurrence and geodatabase mapping of the anti-inflammatory drug diclofenac (DCL) and the natural (17-beta-estradiol or E2) and synthetic (17-alpha-ethynylestradiol or EE2) estrogenic hormones in Republic of Ireland receiving waters over the period 1999 to 2015. Among these data, 317 samples came from concentration studies, while 205 were from effect-based studies. Monitoring data came from 16 waste water treatment plants (WWTPs), 23 water bodies (including rivers, lakes, marine and transitional waters) and 7 from domestic locations. Out of approximately 1000 WWPTs in the Republic of Ireland, only 16 have been monitored for at least one of these compounds of emerging concern (CECs). Diclofenac is found in treated effluents from 5 WWTPs at levels at least as high as other European WWPTs, and sometime higher. Measurements of E2 and EE2 in WWPT effluents were rare and effluents were more often evaluated for total estrogens; these CECs were generally not detected using conventional analytical methods because of limits of detection being too high compared to environmental concentrations and WFD environmental quality standards. There was good agreement between occurrence of these CEC and regional drug dispensing data in Ireland. Mapping the aforementioned data onto appropriate river basin catchment management tools will inform predictive and simulated risk determinations to inform investment in infrastructure that is necessary to protect rivers and beaches and economic activities that rely on clean water. There is a pressing commensurate need to refine/develop new analytical methods with low levels of detection for future CEC intervention.



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**Contents**



## 1. Introduction

Pollution of European receiving waters containing pharmaceuticals is a ubiquitous phenomenon (Verlicchi and Zambello, 2016; Barbosa et al., 2016; Tiedeken et al., 2017). Until recently environmental regulations worldwide had not required explicit testing of these contaminants of emerging concern in water bodies. However, given concern about contamination of aquatic environment with these substances, legislation such as the Water Framework Directive (WFD) and the Environmental Quality Standards Directive (EQSD) at a European level and associated legislation at a local level has recently begun to acknowledge this problem (Tiedeken et al., 2017; Tahar et al., 2017) The identification of these contaminants and associated analytical methods may inform pressure points and efficacy of appropriate interventions for consideration in future WFD-monitoring programmes and regulations. Pharmaceuticals are a class of emerging environmental contaminants that are widely used in human and veterinary medicine (Tahar et al., 2017). From here on, these substances of emerging concern will be referred to as pharmaceutically active chemicals (PhACs) that includes not just pharmaceuticals but also their pharmaceutically active metabolites/transformation products. This research is important because of the potential toxic effects for aquatic biota and human health that may result from chronic exposure to PhACs (Streck, 2009; Kümmerer, 2009; Kosma et al., 2014). PhACs exhibit wide variation in function, chemical structure and physiochemical properties, making it difficult to generalize about their behaviour, persistence or impact in the environment. PhACs are also designed to be biologically active, have a specific mode of action and to be persistent in the body, meaning they can impact humans and wildlife at trace concentrations which are often hard to detect and quantify using traditional analytical methods (Kosma et al., 2014). A large number of PhACs have been detected in wastewater treatment plants (WWTP) influents and effluents and surface, ground and drinking water worldwide in recent years (Cirja et al., 2008; Streck, 2009; Zhou et al., 2009; Verlicchi and Zambello, 2016). It is now established that throughout the developed world, PhACs are ubiquitous at μg to ng per litre levels in the aquatic environment (Streck, 2009). The impacts of chronic exposure to trace concentrations of many PhACs on wildlife and human health may be severe (Verlicchi et al., 2012); thus, it is critical to limit as much as possible the concentrations of this class of contaminants in our waterways.

Until recently, environmental regulations worldwide had not required explicit testing for any PhACs in water bodies. However given the growing concern about contamination of the aquatic environment with these compounds, legislation has recently begun to acknowledge this potential problem. The WFD requires that all EU member states prepare river basin management plans (RBMPs) to address the many issues relating to water quality and protection in a holistic manner. In response to growing EU concern about the release of untreated PhACs into the aquatic environment, three compounds were included on in the first EU watch list in 2013: diclofenac (CAS# 15307-79-6, hereafter referred as DCL), 17-beta-estradiol (CAS# 50-28-2, hereafter referred as E2) and 17-alpha-ethinylestradiol (CAS# 57-63-6, hereafter referred as EE2) (Barbosa et al., 2016). Annual average environmental quality standard (AA-EQS) were defined for these 3 compounds as being the concentrations defining the boundary between good and moderate WFD status. The respective AA EQS in surface water for DCL, E2 and EE2 are 100 ng/L, 0.035 ng/L and 0.4 ng/L. EE2 and E2 can impact the endocrine system of humans or wildlife (Verlicchi et al., 2012). There are growing fears that chronic exposure to these endocrine disrupting chemicals or EDCs (in bathing or drinking water, for example) may be linked to adverse human health conditions such as declining male fertility, birth defects, and breast and testicular cancer. Similar to PhACs as a whole, EDCs are mainly thought to be transported into the aquatic environment via incomplete removal at WWTPs (Streck, 2009). It is relevant to note that the European Commission implemented decision 495 of 20 March 2015 that expanded substances or groups of substances on the watch list to 10 in the field of water policy (Barbosa et al., 2016). Also, following the timetable for the common implementation of the WFD, the first management cycle ended in 2015, and the second river basin management plan combined with the first flood management plan is due to end in 2021.

A systematic review of these three first EU watch list PhACs in receiving waters was recently published, which reviewed 3945 potentially relevant articles over period 1995 to 2015 publications on uses, sources, monitoring and control measures to produce a EU-wide database (Tiedeken et al., 2017). Overall, European surface water concentrations of DCL are typically below reported annual proposed AA EQS of 100 ng/L, but exceedances frequently occur. E2 and EE2 surface water concentrations are typically below 50 ng/L and 10 ng/L respectively, but these values greatly exceed the proposed AA EQS values for these compounds (0.4 and 0.035 ng/L respectively). However, levels of these PhACs are frequently reported to be disproportionately high in EU receiving waters, particularly in effluents at control points that require urgent attention. In addition, the EPA reported in October 2017 that in 42 locations in the Republic of Ireland, sewage is discharged untreated, putting rivers and bathing areas at risk of pollution: 44 of 170 large urban areas did not comply with EU water quality standards (EPA, 2017). The review of Tiedeken et al. (2017) highlighted that there is a pressing need to conduct detailed mapping of the occurrences and control measures for CECs at a national scale that provides a platform for EU orientation so as to inform policy and decision-making on improving and protecting water quality. Thus, the aim of this case study was to evaluate best-published data on these three EU Watch list PhACs so as to geographically map their occurrence in Irish receiving waters and in effluent at WWTPs and to compare with regional drug dispensing data.