Pharmaceuticals and their Transformation Products in Hospital Wastewater and Conventional Wastewater Treatment Plants

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1. Introduction

Pharmaceuticals (pharma) are extensively used and introduced into our wastewater where inadequate removal leads to release into surface waters. The effects of wastewater treatment on pharma behaviour is not fully understood – especially the formation and fate of degradation products. Advanced treatment (chemical oxidation, disinfection) and natural degradation (photolysis, biodegradation) may form toxic and/or bioactive products.[1] Hospitals have been identified as a major point-source for pharma entering municipal sewers [2], and rural hospitals are of concern as subsequent treatment may be carried out with smaller, less advanced wastewater treatment plants (WWTPs). Therefore, to protect water quality and aquatic ecosystems, research is needed to investigate pharma degradation, product distribution and persistence in wastewater in rural communities.

In this study pharma and transformation products were characterised in hospital wastewater, and pharma behaviour at separate stages of the wastewater treatment process was determined. Target compounds included: paracetamol, diclofenac and ibuprofen (analgesics/anti-inflammatories), clarithromycin and trimethoprim (antibiotics), carbamazepine and fluoxetine (psychiatric drugs) and 17α-ethynylestradiol (synthetic hormone). Several of these compounds are included on European and UK drinking water legislation control lists (Water Framework Directive, Environmental Quality Standards Directive) [3], highlighting the importance of characterising fate and transport in wastewater.

2. Materials and methods

Samples were collected over seven weeks from from Caithness General Hospital (Wick, UK) and four sites within the Wick WWTP: raw influent, primary sample, secondary sample and final effluent. Samples taken from the primary and secondary stage of wastewater treatment were taken during the process (i.e. not as effluent). A solid phase extraction method and liquid chromatography-tandem mass spectrometry (LC-MS/MS) analysis technique were developed for quantitation of target compounds. Deuterated internal standards of each target compound were spiked into all samples prior to solid phase extraction to calculate pharma recoveries. High resolution Orbitrap LC-MS was used for screening of suspected degradation products and non-target analysis of all samples. Water quality parameters that were monitored included pH, conductivity, turbidity, suspended solids, dissolved organic carbon and dissolved inorganic carbon.

3. Results and discussion

Through LC-MS/MS analysis, pharma were detected in varying concentrations in all samples, Figure 1. Average concentrations ranged from 2.11 ng/L (diclofenac, secondary sample) to 4030 ng/L (paracetamol, primary sample). Paracetamol and ibuprofen were detected in highest concentrations (exceeding graph axis): 1380 ± 450 ng/L and 2070 ± 1900 ng/L (hospital outflow), 3800 ± 1000 ng/L and 3180 ± 730 ng/L (raw influent), 4030 ± 420 ng/L and 1840 ± 980 ng/L (primary sample), respectively. 17α-ethynylestradiol was only detected in raw influent and primary samples above the limit of quantitation (0.80 ng/L). The fractional removal was calculated for each compound from influent concentrations compared to concentrations at separate stages, Figure 2. This indicated the change in pharma concentrations during the treatment process, with the far right of the diagram showing the percentage from raw influent that is discharged. The antibiotics trimethoprim and clarithromycin were recalcitrant to removal, with final effluent concentrations exceeding influent concentrations (>200% initial concentration in final discharge).

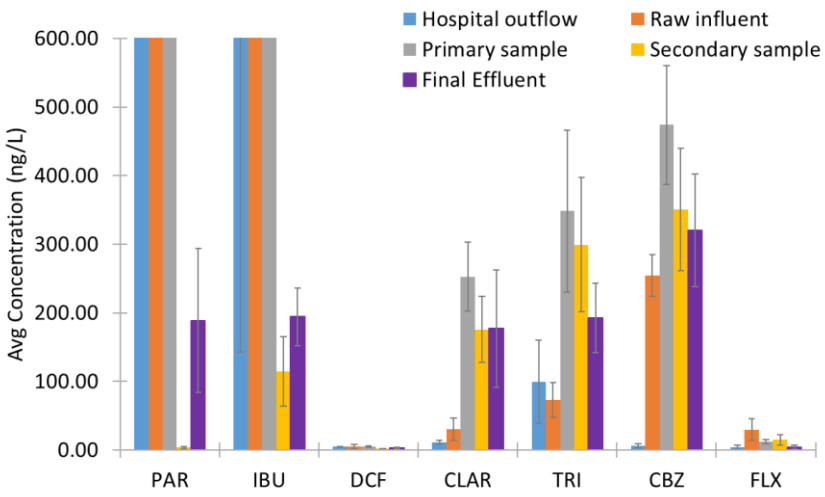

Figure 1: Average (avg) concentrations of pharmaceuticals in ng/L detected at separate stages of the wastewater treatment process. Error bars indicate standard deviation (n=7). PAR = paracetamol, IBU = ibuprofen, DCF = diclofenac, CLAR = clarithromycin, TRI = trimethoprim, CBZ = carbamazepine, FLX = fluoxetine.

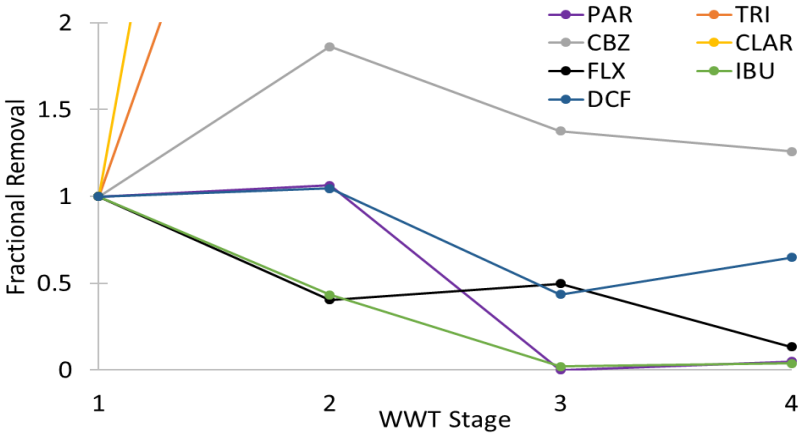

Figure 2: Fractional removal of pharmaceuticals at separate stages of the wastewater treatment process. 1 = raw influent, 2 = primary stage, 3 = secondary stage, 4 = final effluent.

4. Conclusions

In this study the removal and transformation of pharma in a rural WWTP was investigated, as well as the presence of pharma degradation products in hospital wastewater. Concentrations were determined with LC-MS/MS analysis, and fractional removal at separate stages indicated that conventional methods employed at Wick WWTP (UK) are unable to fully remove these compounds. High resolution mass spectrometry with Exactive Orbitrap LC-MS was used for identification of pharma degradation products in all samples (results not included), which enabled elucidation of pharma transformation behaviour in the WWTP. A risk assessment was carried out which suggested that paracetamol, fluoxetine, diclofenac, clarithromycin and 17α-ethynylestradiol are of most environmental concern. The distribution and degradation of these compounds in WWTPs and effluent-receiving surface water should be further investigated.

5. References

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