Abstract

<u>Title</u>

Spatial distribution of pharmaceutical pollution within a river catchment

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Introduction

Presented are the results of a sampling campaign investigating the spatial distribution of pharmaceutical micropollutants, in the upper and middle reaches of a river catchment. The River Almond and its tributaries receive effluent from multiple sewage treatment works (STW), using trickling filters and activated sludge technologies. Pharmaceutical concentrations in surface waters depend on the pollutant load as discharged from multiple point sources (STW effluent), environmental degradation and / or sequestration during transport and the available dilution provided by the River Almond and its tributaries. There are 20 distinct Water Bodies, in the sense of the River Basin Management Plan, within the River Almond catchment. Under the Environmental Quality Standards (EQS) Directive (2008/105/EC) (1), all water bodies must comply with EQS. Following the inclusion of several pharmaceutical products on a 'watch list' (2) and with a real possibility of pharmaceuticals being identified as Priority Substances in the future, a better understanding of the environmental distribution and fate of such pollutants is desirable.

Materials and Methods

Daily grab samples were taken at 7 locations within the catchment for 4 consecutive days in June 2014, between 10:30am and 2pm each day, during dry weather. The locations were chosen to generally build up a picture of concentrations across the catchment and with the specific objectives to 1) compare river loads and concentrations upstream, 400m downstream and 10km downstream from a trickling filter (TF) plant (capacity 5000 PE) in a small stream, 2) investigate the effect of a larger Conventional Activated Sludge (CAS) STW (capacity 84,000 PE) and 3) generate an understanding of variation in a spatial context. In order to be able to calculate load, a depth profile was taken at each river location and flow velocity readings were taken daily using a simple handheld flow meter (Geopacks MFP51). Alongside conventional water quality parameters, concentrations for 20 pharmaceutical compounds were determined by using a Thermo Scientific Q Exactive orbitrap mass spec with a Dionex Ultimate 3000 LC system; below we report results for Atenolol, Bezafibrate, Carbamazepine, Lidocaine and Clarithromycin.

Results and Discussion

All compounds were found on most days at all locations, apart from the one upstream from all STW, which - as expected - did not show any pharmaceutical pollution. Concentrations at other locations in the river were generally measurable but below $1\mu g/l$. Clarithromycin, Bezafibrate, Lidocaine and Carbamazepine showed some variation across the days, generally up to a factor 6, whereas Atenolol showed the most variation across the days as this compound was not detected every day.

In respect of objective 1), where concentrations were measured at two sites 10km apart on a small stream, which is a tributary to the River Almond. Downstream concentrations were expected to be lower than upstream due to dilution and possibly environmental degradation or sequestration. The mean concentrations of Atenolol and Clarithromycin were a factor 5 (Atenolol) and 6 (Clarithromycin) lower at the downstream location. The mean concentration for Carbamazepine however was only slightly (30%) reduced downstream. For Bezafibrate, concentrations were also reduced by 30% on 3 days, but on the 4th day the downstream location concentration was below LOQ. Unexpectedly, Lidocaine was found in considerably higher concentrations at the downstream location. A possible explanation is the presence of other possible inputs: the upstream location is just downstream from a STW serving just under 5000 people. Although no other STW inputs are present along the stretch, there are a number of other authorised discharge points (e.g. septic tanks) in the tributary's catchment. Whilst the total population served by these is likely to be small compared to that served by the STW, it is possible these have contributed to the downstream concentrations. As Lidocaine is also used in veterinary practice, farm run-off may also have contributed to the higher concentrations. Further data on the nature and size of the authorised discharges into the river is currently being sought. Two smaller tributaries join the investigated stretch of water between the two sampling points, so that dilution will have played a role in the reduction of concentrations.

In respect of objective 2), in samples taken upstream and downstream from the large STW (capacity 84,000 PE) Atenolol was only detected on one day at the upstream sampling point and on three days at the downstream sampling point, but all samples at both points contained Bezafibrate, Carbamazepine, Clarithromycin, and Lidocaine. Concentrations for these compounds on each of the sampling days were similar, with the RSD for each compound between 35% and 57% at the upstream location, and between 13% and 34% at the downstream location. The mean concentration for Bezafibrate downstream from the STW was 6 times higher than upstream; for Carbamazepine, Clarithromycin and Lidocaine the increase was by a factor 1.6-1.8. This increase is less than expected, as the large STW has a capacity over 1.5 times the total capacity of the smaller STWs discharging into the catchment before the upstream sampling point, and the large STW also serves a hospital.

Conclusions

From the results, it is clear that pharmaceutical pollutants can be transported over a long range. Some compounds, such as Atenolol, appear to be degraded or sequestered considerably along a 10km stretch of river, but Carbamazepine is not, although the influence of private sewage discharges must be investigated further. Despite multiple STW discharging into the River Almond, it is the smaller tributary, which receives effluent only from one relatively small STW, that shows the highest levels of pharmaceutical pollution due to low available dilution. The high levels of Lidocaine apparently not issuing from any STW remind us that other sources of pharmaceutical pollution should not be ignored.

1. European Parliament (2008) Directive 2008/105/C of the European Parliament and of the Council on 16 December 2008 on environmental quality standards in the field of water policy. Council of the European Union 16/12/2008

2. European Parliament (2013) Surface waters: 12 new controlled chemicals, three pharmaceuticals on watch list. Press Release Plenary Sessions 01072013 edn, EU.