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Tracer tests and uncertainty propagation to design monitoring setups in view of pharmaceutical mass flow analyses in sewer systems

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ABSTRACT

The development of a strategic approach to manage pollution of surface waters with pharmaceutical residues is in centre of interest in Europe. In this context a lack of reliable standard procedures for sampling and subsequent assessment of pharmaceutical mass flows in the water cycle has been identified. Authoritative assessment of relevant substance concentrations and flows is essential for environmental risk assessments and reliable efficiency analysis of measures to reduce or avoid emissions of drugs to water systems. Accordingly, a detailed preparation of monitoring campaigns including an accuracy check for the sampling configuration provides important information on the reliability of the gathered data. It finally supports data analysis and interpretation for evaluations of the efficiency of measures as well as for cost benefit assessments. The precision of mass flow balances is expected to be particularly weak when substances with high short-term variations and rare upstream emissions are considered. This is especially true for substance flow analysis in sewers close to source because of expectable highly dynamic flow conditions and emission patterns of pollutants.

The case study presented here focusses on the verification of a monitoring campaign in a hospital sewer in Luxembourg.

The results highlight the importance for a priori accuracy checks and provide a blueprint for well-designed monitoring campaigns of pharmaceutical trace pollutants on the one hand. On the other hand, the study provides evidence that the defined and applied continuous flow proportional sampling procedure enables a representative monitoring of short-term peak loads of the x-ray contrast media iobitridol close to source.

1. Introduction

Currently, the development of a common strategic approach to manage the pollution of pharmaceutical residues in water bodies is of high priority in Europe. For this reason the European Commission had to suggest a related strategy until September 2015. The European Commission will further propose measures to be executed on European level as well as on the level of the member states to address the environmental impacts of pharmaceutical products by 14th September 2017 (EU, 2013). In particular for substances currently listed on the so-called watch list, like diclofenac, measures have to be proposed to reduce emissions to the aquatic environment. The proposal will include the needs of public health and the cost effectiveness of measures. In this context the study on the environmental risks of medicinal products elaborated for the NGO Executive Agency for Health and Consumers provides important information to support decisions on European level (BIO Intelligence Service, 2013). The final report of the BIO Intelligence Service, 2013 identified considerable gaps of knowledge with respect to the occurrence of pharmaceutical residues in surface waters. Furthermore, the report addresses the lack of reliable and proven concepts for trustworthy assessments of pharmaceutical substance flows.

Authoritative data on relevant substance concentrations and flows is essential for a reliable efficiency analysis of measures to reduce or avoid emissions of pharmaceutical residues to water systems. Accordingly, this is also an important basis for a strategic approach tackling the issue of pharmaceutical residues in the aquatic environments. In this context, detailed data of substance flow contributions of different sources in a sewer system provide

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important information for a future emission management of relevant pollutants including a source classification framework (Holten et al., 2012).

However, the monitoring close to sources in sewer systems is challenging because of highly variable flows and pollutant concentrations. The latter applies to both macropollutants (e.g. COD, TSS, N) and micropollutants (e.g. heavy metals and micropollutants like pharmaceuticals). The dynamic behaviour of dry weather flow conditions close to source is very much linked to diurnal routines involving working processes and human habits usually corresponding to minimas of flows and pollutants concentrations at night. This is shown by Almeida et al. (1999) for diurnal patterns of flow and macropollutants focusing on the example of a dwelling house of about 100 inhabitants. Moreover, for x-ray contrast media and cytostatics in hospital sewage a significant diurnal variation of concentrations was observed by Weissbrot et al. (2009). Therefore, a detailed preparation of monitoring campaigns in sewer systems close to source is essential to gather accurate information on volume and substance flows.

Ort et al. (2010) state that well-designed monitoring campaigns including an accuracy assessment of the sampling configuration are very rare. Especially for monitoring campaigns close to emission sources with relatively high dynamic behaviour a precursory assessment of sampling uncertainty is important.

If significant changes of flow and concentrations are expected it is generally recommended to do volume- or flow-proportional sampling instead of ordinary time-proportional sampling. Consequently, reliable concentration data in a composite sample can be gathered (Ort and Gujer, 2006). Even higher accuracy can be reached by continuous flow-proportional sampling. Ort and Gujer (2006) suggest a continuous flow-proportional sampling method based on ISO (1992). The approach involves the monitoring of the flow rate of the investigated medium and the real-time-control of the sampling flow accordingly.

Against this background, the study at hand suggests a robust verification method of continuous flow-proportional sampling schemes configured to monitor persistent micropollutants with highly dynamic concentration in wastewater. The approach was applied to validate and to prepare a monitoring campaign in the sewer of the Centre Hospitalier Emile Mayrisch in Esch-sur-Alzette (Luxembourg). The hospital has a capacity of 400 beds and about 38,500 stationary patients (ca. 30% of all patients) stayed in the hospital for about 4 days in 2014. For the sampling campaign, representative 24-h composite samples were generated. The subsequent goal was to verify the effect of a possible separate collection and disposal of the x-ray contrast media iobitridol (CAS Number: 136949-58-1) from the radiology department. The impact of the source control of iobitridol was evaluated based on the achieved reduction of mass flow at both points of the sewer, the discharge point of the hospital and the influent of the connected wastewater treatment plant. To simulate emission, transport and sampling a tracer test, as main element of the proposed approach, was applied on-site the hospital.

Herrmann et al. (2015) state that the contribution of health institutions like general hospitals, psychiatric hospitals and nursing homes to emissions of pharmaceutical residues to waste water systems is very low compared to households on national level. Nevertheless, health institutions are identified as major sources of specific substances and of mixtures of numerous compounds on high concentration levels (Herrmann et al., 2015; Mendoza et al., 2015). Mendoza et al. (2015) for instance found that highest substance concentrations in hospital sewage are caused by iodinated X-ray contrast media (ICM).

Weissbrodt et al. (2009) investigated loads of ICM and cytostatics in a hospital sewer. They implemented a volume-proportional sampling, taking a sample of 75 ml each time 2 m^3 sewage passed the sampling location. This resulted in a relatively long average sampling interval of 8min. Finally, 18 h-composite samples taken during the day and 6 h-composite samples taken at night were mixed flow-proportional to generate 24 h-composite samples for ICM analyses. The uncertainty of average concentrations found in composite sample for this sampling scheme was estimated based on the approach by Ort and Gujer (2006). For 2–5 patients excreting a specific substance and causing about 18 toilet flushes per day this results in an uncertainty of approximately ±50%.

The goal of the sampling configuration described here was to enable a much more accurate load balancing.

2. Materials and methods

2.1. Boundary conditions – the fate of iobitridol

The ICM iobitridol is the active compound in the product Xenetix and is a highly polar and persistent substance which is not or very poorly removed in conventional wastewater treatment plants. After application, 99% of iobitridol is excreted via urine within 18 h while 50% is excreted within the first 2 h (information provided by the manufacturer of Xenetix Guerbet, Villepinte, France). In this context a separate collection of iobitridol contaminated urine seems to be an efficient measure at source to reduce or avoid emissions to the environment.

The expected number of patients who received iobitridol was 25 per day. This included 80% of ambulant and 20% of stationary patients. Since it was assumed that predominantly stationary patients contribute to the iobitridol load in the hospital sewer only 5 patients per day were taken into account. Moreover, it was assumed that stationary patients excrete 99% of iobitridol the first five times they urinate. Consequently, 25 significant load pulses of iobitridol were expected to enter the hospital sewer system mixed within the volume of maximum two consecutive toilet flushes.

2.2. Sampling configuration

An essential precondition for flow proportional sampling is an accurate monitoring of flow rates of the observed medium. In the case study presented here the monitoring of flow rates and substance concentrations was carried out in two manholes of the hospital sewer system (see Fig. 1). The latter connects the hospital to the municipal sanitary sewer system of the city of Esch-sur-Alzette. The aim was to gather most reliable flow rates to control the flow proportional sampling and to finally target high accuracy of load balancing. In that regard it was assumed that there is no leakage in the upstream sanitary sewer system and that flow volumes observed in the manholes correspond to the water consumption of the connected hospital departments.

A rectangular thin plate weir was installed in each manhole to measure sewage flow rate on the one hand and to retain enough volume of wastewater as pump sump to feed a pilot treatment plant. The continuous flow-proportional sampling was done in both inlets (connected with each of the manholes) of the pilot facility. The flow rates of both inlets were constantly 2 l/min. Due to the distances between the manholes and the pilot facility the flow times from manholes to the sampling point were 5.1min (manhole 1) and 8.7min (manhole 2). The sampling control took into account the flow times as time delay in the sampling procedure.

2 real-time controlled peristaltic pumps Masterflex P/S (Thermo Scientific) were used to collect flow proportional samples from both pilot inlets. The samples were stored in refrigerated glass