Identification of micropollutants in sewage treatment facilities discharges by using suspect screening strategies based on regulatory databases

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Abstract

Discharges from sewage treatment facilities are a major pathway of organic micropollutants to the aquatic environment. However, the existing target analysis methodologies only allow the detection of a very small fraction of the substances present in wastewater samples. The application of suspect screening, with a suspected screening list based on prior information but with no reference standards, greatly increases the list of substances that can be identified. In the present study a suspect list was built based on the hypothesis that regulatory databases can assist in the prioritization of potentially relevant substances. Therefore, we used the Swedish Chemical Agency database to prioritize substances present in wastewater effluents and surface water by using different criteria including (i) the occurrence on the market, (ii) the consumed tonnage, and (iii) the use pattern. The final list contained ~200 organic micropollutants (with a high ratio of industrial chemicals) and was used to identify the prioritized substances in wastewater.

Keywords: Micropollutants, Suspect screening, Regulatory databases.

1. Introduction

The presence of micropollutants (MPs) is relevant for water quality and may trigger unwanted ecological effects. MPs originate from different point and diffuse sources and enter water bodies via different flow paths (Eggen *et al.*, 2014). Discharges from wastewater treatment plants (WWTPs), in which several MPs are not or only partially removed, have been shown to be a major pathway of organic MPs to the aquatic environment (Luo *et al*., 2014). Target analysis methodologies allow only the detection of a very small fraction of occurring substances, due to the lack of reference standards and/or knowledge about the presence of organic MPs. However, advances in high resolution mass spectrometry (HRMS) have opened up new windows of opportunity in the field of complex samples analysis (Schymanski *et al.*, 2014). The application of suspect screening, with suspected substances based on prior information but with no reference standard, greatly increases the list of substances that can be identified. In the present study, a *smart suspect list* was built containing 200 potential MPs based on the hypothesis that regulatory databases can assist in the prioritization of potentially relevant substances. Therefore, we used the Swedish Chemical Agency (KEMI) database (*The Swedish Products Register, 2015*) to prioritize substances present in wastewater effluents and surface water by using the following criteria: (i) the occurrence on the market, (ii) the consumed tonnage, and (iii) the use pattern. These compounds were screened in influent and effluent of real wastewater from different Swedish WWTPs with both industrial and domestic profiles. The main objective was to determine if these potential previously non-detected MPs are present in the aquatic environment at relevant levels and hence their presence should be monitored in more detail.

2. Materials and methods

2.1. Sampling collection

Influent and effluent 24-hours composite samples were taken from the WWTP of Uppsala (Kungsäangverket). This WWTP serves 172,000 persons (150,000 population equivalent). The wastewater treatment steps at this plant include mechanical treatment and primary sedimentation, biological treatment using activated sewage sludge with nitrogen removal, chemical treatment by addition of iron chloride and a final lamella sedimentation treatment to remove particulate matter. This WWTP receives two different influents: one from the center and east of the city with a clear domestic profile and other one from the west with an industrial profile. Sampling was also carried out in the WWTPs of Stockholm (800,000 population equivalent) and Västerås (150,000 population equivalent).

2.2. Sample treatment and analysis

Sample extraction was carried out using a slight variation of the protocol previously described by Gago-Ferrero *et al.* (Gago-Ferrero *et al.*, 2015). Solid phase extraction (SPE) was conducted for 100 or 200 mL (influent and effluent, respectively) using four different SPE materials simultaneously in an in-house cartridge (i.e. Oasis HLB, Isolute ENV+, Strata-X-AW and Strata-X-CV) to achieve sufficient enrichment for a very broad range of compounds. Samples were further analyzed using ultra performance liquid chromatography (UHPLC) system coupled to a G2S Xevo quadrupole-time-of-flight (QTOF) mass spectrometer (UHPLC-HRMS, Waters).

3. Results and discussion

3.1. Suspect database and suspect processing

The suspect list was built by using the regulatory database of KEMI, which includes industrial chemicals that are consumed in Sweden (The Swedish Product Register, 2015). Prioritization was based on factors such as the occurrence on the market, the consumed tonnage and the use pattern, through the evaluation of different exposure index during 1992 to 2014. The initial data base contained about 23 000 substances (Not published, only for internal prioritization and research). We prioritized ~200 organic MPs (with a high ratio of industrial chemicals) by using the different exposure index. These substances have potentially high chances to be present in the wastewater. For most of the selected compounds there was a lack of literature regarding their presence in the aquatic environment. Therefore it is highly interesting to screen for their potential occurrence. The tentative identification of the suspects was based on the evaluation of criteria including mass accuracy, isotopic pattern, chromatographic retention time plausibility and a deep study of the mass spectrometry (MS) obtained spectra, including comparisons with MS libraries, following a workflow previously developed by Gago-Ferrero *et al*. (Gago-Ferrero *et al*., 2015). Figure 1 shows schematically the main steps followed to reach the tentative identification of the evaluated suspects.

Samples were evaluated in both positive and negative electrospray mode (ESI(+) and ESI(-), respectively) and a high ratio (>40%) of hits (compounds passing the ion intensity / peak area filter, the mass accuracy threshold, the isotofic fit threshold and with a plausible retention time) was obtained. However, it does not mean that the compounds are tentatively identified. A deep study of the HRMS spectra is necessary to reach that point. Several compounds were tentatively identified in the evaluated effluent wastewater samples. One example can be found in dibutyl phosphate. This compound can be used as a precursor for antistatics, as a mould release agent in polyurethane applications and, as a non-volatile acidic catalyst soluble in organic media. It is also a phosphorous flame retardants metabolite (Alves *et al*., 2017). Other Organophosphorus compounds with industrial applications were also determined including the mono-n-butylphosphoric acid, hexadecyl dihydrogen phosphate or dipentyl hydrogen phosphate. To the author's best knowledge for the three last compounds this is the first evidence on its presence in effluent wastewater. It is noteworthy that these substances are not biodegradable (European Chemicals Agency) and they are being released into the aquatic environment Results also showed a high presence of compounds containing sulfur. Several alkylbenzenesulfonates were tentatively identified showing high intensities in the chromatograms. One example can be found in the dodecyl benzenesulfonate. This compound is used as a surfactant. It is usually produced as a mixture of related sulfonates. It is an important component of laundry detergents, among other uses.

3.2.Identification of the suspects

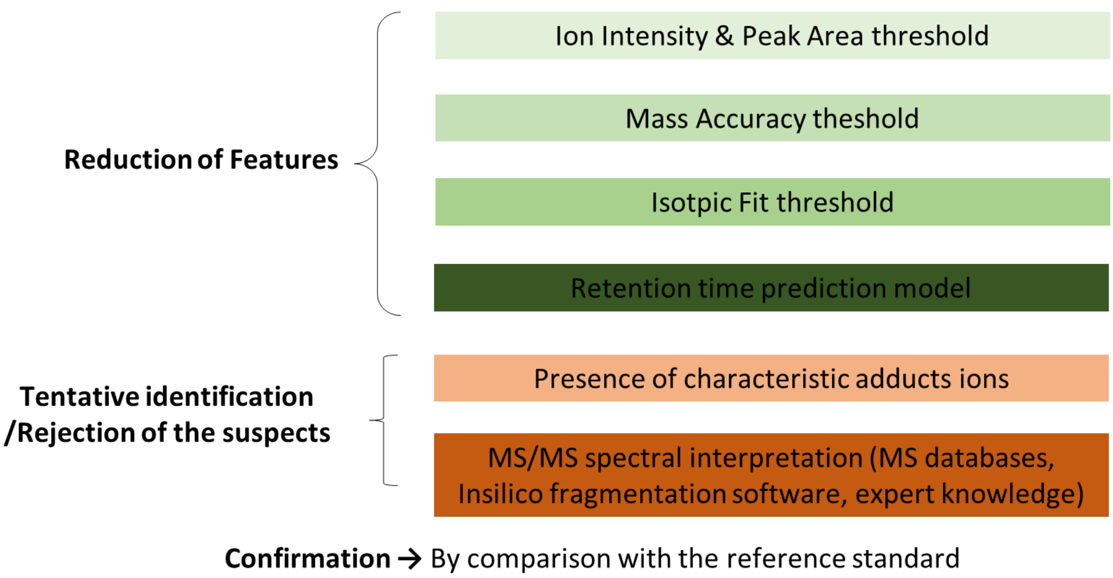

Figure 1 Suspect screening flowchart

The compounds detected in effluents were mostly also determined in the corresponding influents, with intensities in the same range or higher. It indicates that their industrial and/or urban use is the main source of entry into WWTPs and their partial or non-removal is the reason of their presence in the effluents. An exception can be found in dipentyl hydrogen phosphate, which is present in all the effluents but not in the corresponding influents and could be a degradation product of the flame retardant tripentyl phosphate. The results seems to indicate that regulatory databases are efficient tools to prioritize potentially hazardous compounds with high possibilities of being present in the environment, for which little or null attention have been dedicated. Thus, regulatory databases-based suspect screening approaches can help to expand the knowledge about the presence and behavior of MPs in the aquatic environment.

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