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Selection of organic process and source indicator substances for the anthropogenically influenced water cycle

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HIGHLIGHTS

- Proposal of individual micropollutants for assessment of anthropogenic influences.
- Source indicator substances for domestic wastewater, urban run-off and agriculture.
- Process indicator substances for natural and engineered processes.

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ABSTRACT

An increasing number of organic micropollutants (OMP) is detected in anthropogenically influenced water cycles. Source control and effective natural and technical barriers are essential to maintain a high quality of drinking water resources under these circumstances. Based on the literature and our own research this study proposes a limited number of OMP that can serve as indicator substances for the major sources of OMP, such as wastewater treatment plants, agriculture and surface runoff. Furthermore functional indicators are proposed that allow assessment of the proper function of natural and technical barriers in the aquatic environment, namely conventional municipal wastewater treatment, advanced treatment (ozonation, activated carbon), bank filtration and soil aquifer treatment as well as self-purification in surface water. These indicator substances include the artificial sweetener acesulfame, the anti-inflammatory drug ibuprofen, the anticonvulsant carbamazepine, the corrosion inhibitor benzotriazole and the herbicide mecoprop among others. The chemical indicator substances are intended to support comparisons between watersheds and technical and natural processes independent of specific water cycles and to reduce efforts and costs of chemical analyses without losing essential information.

1. Introduction

The number of individual chemical compounds in use is increasing due to progress in chemical and pharmaceutical research and development. This, likely, leads to an increasing diversity of chemicals that are regularly released and that contaminate the environment and the water cycle. As a consequence, the analytical effort to detect all relevant contaminants in the environment is increasing. Progress in analytical techniques partly compensates for this by more efficient methods but also leads to an

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increasing number of organic micropollutants (OMP) that are detected in the aquatic environment.

On this basis, the selection of a limited set of OMP that is indicative for either a certain source of contamination or the performance of a certain removal process would facilitate data acquisition, processing, evaluation and interpretation.

In the literature several studies are found that identify or apply indicator substances. A selection of representative OMP with regard to physico-chemical and structural properties has been provided for drinking water treatment by Jin and Peldszus (2012). Quantitative relationships of OMP structure and property (QSPR) or activity (QSAR) have been applied to predict the behavior of OMP in treatment processes (Magnuson and Speth, 2005; Lei and Snyder, 2007; Yangali-Quintanilla et al., 2010). Reemtsma et al. (2006) introduced the water cycle spreading index that provides information on the fate of OMP. A categorization of OMP for surface waters was developed by Götz et al. (2010b). Benzotriazole, carbamazepine, diclofenac, mecoprop and sulfamethoxazole have been proposed as indicator substances for conventional and advanced wastewater treatment with ozone or activated carbon in Switzerland (Götz et al., 2010a). Drewes et al. (2013) discussed a strategy for compound selection for water reclamation that also considers toxicological relevance. Indicators for various substance classes have been discussed with regard to public health significance (Pal et al., 2014). A list of OMP with consideration of risks was proposed by Helwig et al. (2013) for the monitoring of hospital effluents. However, existing selections or categorizations focus on specific compartments of the water cycle or still include large numbers of OMP.

The selection of indicator substances has been identified as an important task in the German funding program RiSKWa (risk management of emerging compounds and pathogens in the water cycle) and its individual projects (Grummt et al., 2013; Huckele and Track, 2013; Jekel et al., 2013; Triebskorn et al., 2013). A group of experts from different joint projects within evaluated OMP as indicator substances with regard to specific functions, relevance and interpretation, as indicated below. Although the selection presented in this contribution is influenced by a European point of view, most indicator substances are used worldwide and appear appropriate on a global scale. Harmonized indicator substances would be useful for the determination of anthropogenic influences in the aquatic environment and for evaluation, monitoring and control of technical processes.

The selection and evaluation of a limited number of specific indicator substances might be useful not only for scientists but also for authorities and agencies, water suppliers and wastewater dischargers, companies, consultants and other stake holders dealing with water quality.

2. Requirements for indicator substances

Indicator substances should be representative of a group of OMP with similar characteristics with respect to application, source, physicochemical properties or reactivity. Basically, indicator substances may either be source indicators or process indicators. Ecotoxicological and human health risks are intentionally excluded. Based on this, indicators should comply with as many of the following criteria as possible:

(1) The sources of indicator substances should be known, distinct and common and they should be continuously released into the water cycle. Certain OMP show significant seasonal, diurnal or other temporal variations (e.g. variation of X-ray contrast media depending on the day of the week) or strong spatial differences. These characteristic patterns should be considered in sampling procedures and data interpretation.

(2) Indicator substances should occur continuously (high detection frequency) in the system studied and in concentrations significantly above the limit of quantification of commonly used analytical methods, despite dilution in the environment. Hence, the total emissions of an indicator substance should be high enough to result in quantifiable concentrations despite dilution. OMP with only sporadic occurrence are not useful.

(3) Indicator substances should be detectable at low concentrations with comparably low effort by widely available methods. The quantitative determination of indicator substances is mostly based on liquid-chromatography coupled to mass spectrometry. Due to the typical limit of quantification in the magnitude of approximately 10 ng L^{-1}, environmental concentrations of indicator substances should be well above 50 ng L^{-1}. Similarly, Dickenson et al. (2011) applied the detection ratio (defined as quantified concentration divided by the limit of quantification) as selection criteria for indicator OMP.

(4) The fate of indicator substances in the processes encountered in all natural compartments of the water cycle (e.g. photolysis, biodegradation, adsorption and others) as well as in treatment processes should be well understood.

(5) The removal in conventional wastewater treatment should be known for the indicator substances selected for the evaluation, comparison, monitoring and control of advanced treatment processes.

(6) Source indicators require a comparably high polarity, a low sorption tendency and a high persistency towards chemical and biological attenuation processes.

(7) Process indicators should exhibit a defined reactivity/behavior towards the respective process.

Intentionally the indicator substances proposed in this study have not been selected on the basis of their toxicological or ecotoxicological properties, because the indicators are used either as source indicators or as process indicators, but not as indicators for water quality or biological effects.

An overview of the sources and processes considered in this study is given in Fig. 1. Industrial discharges were excluded since they are very specific for different industries. Hospitals as potential ‘hotspots’ for the discharge of certain pharmaceuticals are included in households, since they usually discharge into the same sewer system and are thus treated together. Although the consumption of pharmaceuticals in hospitals is elevated, their excretion may

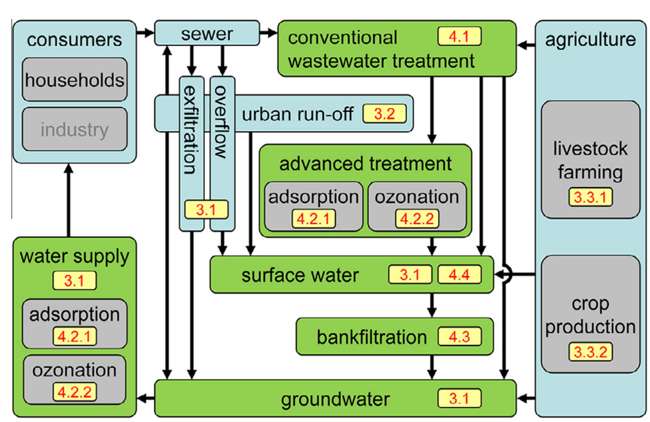

Fig. 1. Sources (blue) and processes (green) in an anthropogenically influenced water cycle for which indicator substances are proposed. The numbers indicate the respective sections in this article. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)