Developing tools for non-target analysis and digital archiving of organic urban water pollutants

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Akademisk avhandling

som med vederbörligt tillstånd av Rektor vid Umeå universitet för avläggande av filosofie doktorsexamen framläggs till offentligt försvar i KB.E3.03 (Stora hörsalen, Carl Kempe-salen), KBC-huset, Umeå Universitet, fredagen den 2 mars, kl. 10:00. Avhandlingen kommer att försvaras på engelska.

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Abstract
This thesis describes efforts to develop robust methods for the creation and use of digital archives of environmental samples, and proposes guidelines based on the results. Digital archives are repositories that store environmental samples digitally. Traditionally, samples are stored physically in environmental specimen banks over long time periods. However, this has several drawbacks, for example degradation effects and limited accessibility. During the course of my PhD project I developed methods that allow the comprehensive analysis of sewage sludge samples. Sewage sludge is a complex matrix that contains many commercial chemicals. In addition, sewage treatment plants form a link between the human society that generates the sewage and the environment, making sewage sludge a very interesting matrix to analyze. The developed methods enable analysis and subsequent identification of compounds of all sizes and with diverse chemical characteristics. I further explain how unknown compounds can be identified (non-target screening) using mass spectral analysis and several other approaches (e.g. retention indices).

The thesis is divided into three parts. In the first part, Data Generation, I describe the development of sample preparation methods for analyzing sewage sludge with gas chromatography (GC) and liquid chromatography (LC) coupled to high resolution mass spectrometry (HRMS). For the GC approach, two methods involving use of different extraction techniques, solvents, and matrix reduction techniques are presented while for the LC approach different extraction techniques are compared. The methods have been developed to enable the generation of data suitable for digital archiving. In the second part of the thesis, Data Evaluation, I present ways to find and identify compounds of interest. Firstly, time trend analyses provide a way to prioritize pollutants, for example by focusing on pollutants that are increasing with time. Thousands of compounds with significant time trends were detected and several hundred of them were tentatively identified. Compounds with strong increasing trends included, for example, UV-filters from sunscreens. Secondly, a new retention index system for comprehensive two dimensional chromatography (GC×GC) is introduced to characterize compounds in terms of their retention times in the second dimension. The new retention index system is based on co-injection of polyethylene glycols and was validated for various compounds of diverse classes. Thirdly, I tested different ways to predict GC×GC retention times or indices. Those methods include a multivariate prediction (PLS) approach using molecular descriptors, which proved to be the best approach, and use of commercially available software. The last part of my thesis, Data Archiving, discusses requirements to create digital archives and how they can be used. Here I present the current state and options for archiving data files, and give recommendations for each step, from sample collection, through instrumental analysis to storage of the final data.

Keywords
Digital archiving, non-target screening, organic pollutants, sewage sludge, GC-MS, GC×GC, LC-MS, time-trend analysis, retention indices, retention time prediction