Development of a novel GC-APCI-QTOFMS methodology for the determination of more than 300 organic compounds in Asopos river water samples

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Abstract
The site of interest of this study is Asopos river which is located in Sterea Ellada, north of Athens, and passes through areas where 20% of total Greece industrial production takes place. The extensive installation of industries in the area near the river, and the uncontrolled disposal of industrial and agricultural wastes into the river, make the water quality of Asopos questionable. The environmental problem of Asopos river basin is known since 1969, due to the detection of high Cr (VI) concentrations in ground and river water samples with potential carcinogenic effects to human health. However, the probable occurrence of industrial and agricultural organic chemicals with unknown toxic effects has not been studied so far. To the best of our knowledge, this is the first environmental monitoring study in Greece including not only the determination of legislated compounds, but also the wide-scope screening of organic chemicals for which no occurrence data exist.
Keywords: River water, Priority pollutants, Emerging Contaminants, Gas chromatographic techniques, GC-APCI-QTOF

1. Introduction

Over the last decade, the development of high resolving power mass analyzers (HRMS) has contributed significantly to the expansion of environmental studies' interest from the restricted determination of priority pollutants to the wide-scope screening of emerging contaminants (ECs). In light of their potential risk to human health and the aquatic environment, action is urgently required. In the ECs analysis field, there is a clear trend toward LC-HRMS as the majority of ECs are more polar, less volatile and thermally instable, and consequently, less GC-amenable. However, many high usage ECs, as well as priority pollutants, are volatile and thermostable, therefore GC-HRMS methods should be developed. So far, less polar and more volatile compounds remain unexploited, pinpointing the need for the establishment of efficient GC-HRMS workflows in order to extend the chemical domain of the applied screening approaches in monitoring studies.

The aim of this study was the development of a novel methodology for the determination of GC-amenable priority pollutants and emerging contaminants in river water samples from Asopos, following both target and non-target screening methodologies.

2. Materials & Methods

Since the chemical domain of the analysis includes compounds with a wide variety of physicochemical properties, a generic sample preparation protocol should be followed.
Several sample preparation methods were tested, including different extraction techniques and initial sample volumes. In particular, the potential scope extension of ISO 28540:2011 (method applied for the determination of PAHs) to a wide variety of volatile and thermostable compounds was investigated. Moreover, the application of solid-phase extraction with different sorbents like C18 (500 mg) and HLB (200mg) was investigated, as well. For the applicability domain evaluation of the non-target GC-APCI-method, performance criteria will be evaluated with spiked samples of a representative group of compounds, for which reference standards are available. The validation dataset is comprised of more than 300 compounds in total, including chemicals from different classes of GC-amenable compounds, like PAHs, PCBs, OCPs and pesticides.
The developed methodology was applied to the analysis of Asopos river samples. So far, 74 river water samples were collected from 2 sampling points, one close to industrial and agricultural activities and one close to the estuaries of Asopos. Two portable autosamplers were used in order to collect 24-hour samples from the river for 30 consecutive days during winter and for 7 consecutive days during spring.

3. Results

The generic method for the determination of GC-amenable emerging contaminants & priority pollutants has been developed and validated. Recoveries and matrix effects were calculated in order to conclude to the optimal sample preparation method. Solid phase extraction with C18 cartridges was selected for the pre-concentration of the analytes and the clean-up of the river samples.

Numerous of compounds, including metolachlor, fluometuron and penconazole have been detected in river water samples. The concentrations of most of the contaminants was significantly higher in the samples withdrawn close to the industrial and agricultural activities.

The overall results will indicate the contamination degree of Asopos river basin due to the occurrence of GC-amenable priority pollutants and emerging contaminants. In addition, the detection trend of the aforementioned analytes will be evaluated on a monthly and seasonal basis.

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