

## GC-MS RESIDUE ANALYSIS OF ORGANIC UV FILTERS IN NATURAL WATERS. CASE STUDIES OF URBAN AND MOUNTAIN WWTPs.

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Nowadays the use of sunscreen products is of superlative importance to protect our skin as well as different products from the deleterious effects of the sun. These formulations usually contain several UV filters in high proportions to provide protection against UVB (280-315nm) and UVA (315-400 nm) radiation<sup>1</sup>. After use, UV filters enter the environment directly, released by swimmers, and indirectly by personal hygiene measures (showering, laundring) but also other sources, as for instance, by leaching from UV radiation-vulnerable surfaces, car polishers, textiles, etc. and ultimately reach wastewater treatment plants (WWTPs)<sup>2,3</sup>. Despite few reports on UV filters removal in water treatments are beginning to become available, much is still unknown. Few studies about toxicity and estrogenic activity of UV filters were reported so far<sup>4,5</sup>, but potential effects in human remain unclear.

The present study aims to develop a new analytical method for the determination of five UV filters in different water matrix and to compare the removal efficiency of four mountain WWTPs in contrast with three urban plants. The five studied UV filters (see Figure 1) are among the 26 organic sunscreen agents currently permitted in the EU (Council Directive 76/768/EEC of 27 July 1976 and amendments)<sup>6</sup>.

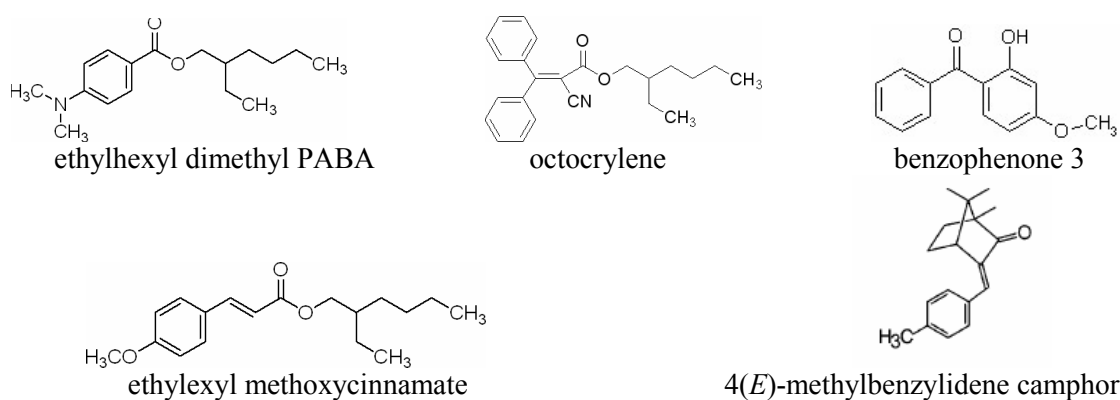


Figure 1

The analytical method applied was based on solid phase extraction (SPE) using C<sub>18</sub> cartridges and further analysis by gas chromatography-mass spectrometry (GC-MS). In order to increase the sensitivity and selectivity data acquisition was performed in selected ion monitoring (SIM) mode. For identification the retention time and the four most intense fragment ions were used. For quantification internal standard calibration was employed (*benzyl cinnamate* as internal standard and *D<sub>15</sub>-musk xylene* as surrogate standard).

The sensitivity of the method expressed as MLODs and MLOQs were in the range 3-570 ng L<sup>-1</sup> and 10-1840 ng L<sup>-1</sup>, respectively, in waste waters (influent and effluent). The intra-day and inter-day precision were satisfactory with relative standard deviations lower than 9 % (using

9 replicates) and lower than 11 % (for 5 different days). Recovery rates higher than 70 % for most compounds were achieved in clean waters and higher than 55 % in waste waters.

The results obtained evidenced the presence of all the investigated compounds in influent and effluent waters from both areas. The presence of the *Z*-isomer of 4-methylbenzylidene camphor in one of the urban WWTPs indicated the change in the stereoisomer composition as consequence of the biotic transformation underwent by this agent during the water treatment process.

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#### References

- (1) M.S. Díaz-Cruz, M. Llorca, D. Barceló, Trends in Anal. Chem. *In Press*
- (2) T. Poiger, H.R Buser, M.E. Balmer, P.A. Bergqvist, M.D. Müller, Chemosphere 55 (2004) 951-963.
- (3) D.L. Giokas, V.A. Sakkas, T.A. Albanis, J. Chromatogr. A 1026 (2004) 289-293.
- (4) S R. Schreurs, P. Lanser, W. Seinen, Arch. Toxicol. 76 (2002) 257.
- (5) T. Butt, T. Christensen, Radiation Protection Dosimetry 91 (2000) 283
- (6) European Commission. Council Directive 76/768/EEC of 27 July 1976 and its successive amendments.  
[http://europa.eu.int/eurlex/en/lif/reg/en\\_ergister\\_133016.html](http://europa.eu.int/eurlex/en/lif/reg/en_ergister_133016.html)