Nontarget screening of halogenated disinfection by-products in swimming pool water by LC-HRMS

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Introduction
Disinfection of swimming pool water with chlorine is worldwide the most commonly used method and is a compromise between hygienic safety and the effects of toxic disinfection by-products (DBPs). A recent study identified more than 100 DBPs in swimming pool water by GC-MS, many of them not previously identified [1]. Much less is known on the polar DBPs. LC coupled with high resolution mass spectrometry enables to determine sum formulae and hence to do screening for unknown compounds. However, the availability of LC-MS libraries and especially entries of transformation products are very limited. Statistical analysis and manual interpretation of mass fragmentation have to be used [2].

Materials and Methods
Water from public swimming pools with different treatment steps and bather loads were taken. The samples were acidified (pH2), pre-concentrated by solid phase extraction on LiChrolut ENV+ by a factor of 5000 and analyzed by LC-ESI-QTOF-MS (Agilent iFunnel 6550). Accurate mass and retention time data were processed in a non-target approach.

LC-Q-TOF Analysis
MS-Fullscan

Data Extraction
Molecular Feature Extraction

Sum Formulae
Generate Formulæ

Statistical Analysis
Mass Profiler

Data Base
Search for suspects

In silico fragmentation
Targeted MS/MS

Identification
Spectral library, MetFrag
Molecular Structure Correlator

Molecular feature extraction

Results

Number of compounds (Score > 70 %)

<table>
<thead>
<tr>
<th></th>
<th>Pool water</th>
<th>Filling water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sum formulae</td>
<td>1800</td>
<td>900</td>
</tr>
<tr>
<td>(C,H,Br,N,O,S)</td>
<td>6400</td>
<td>2700</td>
</tr>
<tr>
<td>≥ 1 chlorine</td>
<td>630</td>
<td>245</td>
</tr>
<tr>
<td>≥ 1 bromine</td>
<td>190</td>
<td>80</td>
</tr>
</tbody>
</table>

Statistical analysis

Pattern Matching
(Mass Profiler Software)
- blue: Compounds in filling water (not relevant)
- red: Compounds in pool water (relevant)

Compounds with molecular features
- 650 down regulated features (filling water)
- 3500 up regulated features (pool water)

Compounds with ≥ 1 chlorine
- 50 down regulated features (filling water)
- 300 up regulated features (pool water)

Degree of unsaturation (DBE) Van Krevelen-Plot

Structure information (MSMS)
for 70 chlorinated compounds (n = 3, Score > 90%)

In-silico fragmentation

Proposed structures with additional fragment information
(Molecular Structure Correlator)

Conclusions and Outlook
- In swimming pool water samples sum formulae of more than 300 halogenated compounds have been found.
- Decreased number of DBE with increasing chlorination degree suggests these compounds as DBPs.
- Halogenation products of preservatives (salicylic acid) and surfactants (sulfonic acid derivatives) were tentatively identified.
- Confirmation of the proposed halogenated compounds requires standards to be generated from available precursors.

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References:

Data base search

Tentative compounds
ID (ChemSpider)
Source
Chloro-2-hydroxybenzoic acid (1) 9075 Preservative
Chloro-2-pyrrolidinylmethylamine (2) 243075 ??
Chloro-methylphenoxy-ethanol (3) 120379 Surfactant?
(Nitro-sulfo-chloro-phenyl)acetic acid (4) no entry Surfactant?

Proposal structures with additional fragment information
(Molecular Structure Correlator)

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