# Screening and Quantitation of Micro-pollutants from Sewage Water in the Process of Bank Filtration Using UHPLC-HRAM

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## Overview

**Purpose:** To show how bank filtration can help to generate a closed water cycle in areas of limited water availability.

**Methods:** Screening for and quantitation of micropollutants was carried out along a transect at the lake Tegeler See in the city of Berlin, Germany.

**Results:** Several contaminants could be detected and quantified, their behavior under different redox conditions was studied.

## Introduction

In the city of Berlin, Germany, drinking water is completely derived from ground water containing large portions of river bank filtrated water. In this study, the barrier function of bank filtration for micro-pollutants was investigated along a transect at the lake Tegeler See in the city of Berlin. The transect consisted of multiple ground water sampling sites between the lake and a water supply well. The derived samples were analyzed using UHPLC – high resolution accurate mass spectrometry, conducting a screening study for contaminants not yet detected in the urban water cycle of Berlin. The lake contains up to 30% of efflux water from a municipal waste water treatment plant and contaminants penetrating the ground water were put into focus in this study.[1]

## Methods

### Sample Preparation

Samples from different ground water probing sites and a ground water well were taken and injected onto the online-SPE system directly.

### Liquid Chromatography

1 mL of sample was injected onto the online-SPE system. For pre-concentration, a C18 column, 2.1 × 20 mm with 12 µm particle size was used. For compound separation, a C18 column, 2.1 × 50 mm with 1.8 µm particle size was used. A gradient formed from water and methanol, both spiked with 0.1% formic acid, was ramped up from 2% B to 95% B in 6.7 minutes. Total chromatographic cycle time including online reconcentration was 15 minutes.

### Mass Spectrometry

Mass spectrometric analysis was run on a Thermo Scientific™ Q Exactive™ Focus hybrid quadrupole-Orbitrap mass spectrometer (Figure 1).

*MS-parameter for screening purposes*[3]
*Full Scan*
- ESI+ and ESI– separately
- R = 70000
- *m/z* 100–1000

*variable Data Independent Acquisition (vDIA)*
- R = 70000
- CE = 30
- *m/z* 100–205, 195–305, 295–405, 395–505, 495–1000

*MS-parameter for quantitative analysis*[1]
*Full Scan*
- polarity-switching (ESI+ / ESI–)
- R = 35,000
- *m/z* 103–900
- internal standards

### Data Analysis

Qualitative and quantitative analysis was done with Thermo Scientific™ TraceFinder™ software; for degradation and transformation product search, Thermo Scientific™ Compound Discoverer™ software was used.

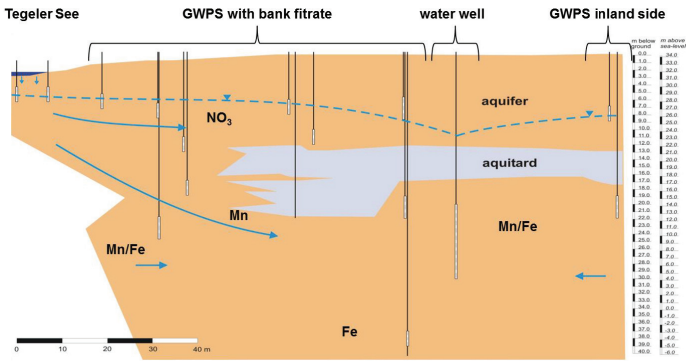
**FIGURE 1. Q Exactive Focus with Thermo Scientific™ EQuan MAX Plus™ Turbo online SPE-system.**

## Results

### Bank Filtration at the Tegeler See

When surface water from a river or lake enters the ground water system, the organic compounds that it contains are degraded in the process, called bank filtration. At the shore of the lake Tegeler See in the city of Berlin, Germany, a series of ground water probing sites has been set up between the lake and a ground water well used to draw raw ground water for the generation of drinking water for the city of Berlin. Figure 2 shows this setup and the conditions found underground that affect the degradation of micro-pollutants in the surface water. Mainly, three different regions can be identified. First, a region with a redox potential of roughly 300 mV, which appears to be nitrate reducing. The second region shows a redox potential of roughly 200 mV and appears to be manganese reducing, while the redox potential of the third lies at roughly 100 mV and tends to be iron reducing.

**FIGURE 2. Schematic sketches of the transect at Lake Tegel. Possible flow paths and the water level are indicated (modified after Massmann et al.[4]).**




GWPS = ground water probing site

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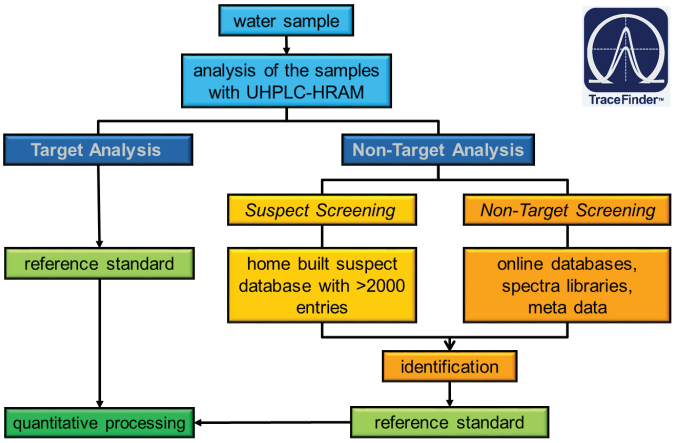
### Suspect Screening

The first step in the investigation was to carry out a non-target analysis of the samples drawn from the ground water probing sites and the ground water well. Figure 3 shows a schematic diagram of the full workflow carried out in this study. Starting with a set of samples, suspect screening was carried out, leading to 260 suspects, of which 94 could be confirmed by using confirmation criteria like isotopic pattern match and matching of known fragments.

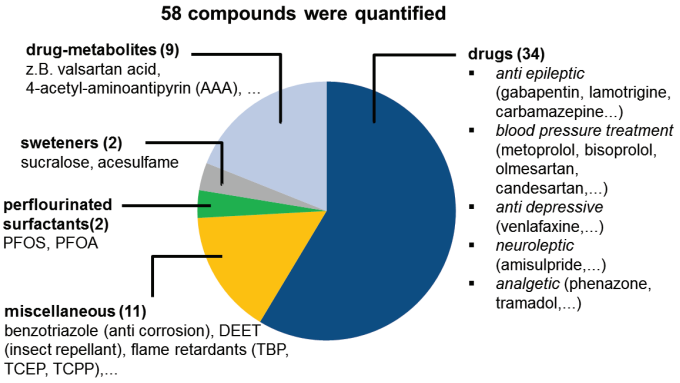
**FIGURE 3. Process of data acquisition and processing for target and non-target analysis; all processing done with TraceFinder 3.3 software.**




### Quantitative Analysis

For these 94 confirmed suspects, reference standards were purchased and run in a dilution series, used for identification and quantitation at the same time. As Figure 4 shows, 58 components could be identified by this approach and could be quantified at the same time.

**FIGURE 4. Result of the quantitative processing of the data**




An important part of the investigation was to determine the degradation behavior of the identified compounds and the evaluation of the ability of the bank filtration process to eliminate these compounds. According to the finding of three regions with differing redox potential, three groups of components could be identified that were predominantly degraded in one of the three regions. Figure 5 shows examples of these three groups and their allocation to the three redox areas underground. The first group of compounds was identified as the one facing aerobical degradation, where the compounds show fast decrease of concentration over the course of the transect and mostly are not detectable in the sample from the ground water well. The second group was identified as the one where the compounds undergo mostly anaerobical degradation and show slower decrease of concentration over the course of the transect, but still show low concentrations in the sample from the ground water well used for drinking water production.

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**FIGURE 5. Different degradation behavior according to different redox condition during the process of bank filtration.**

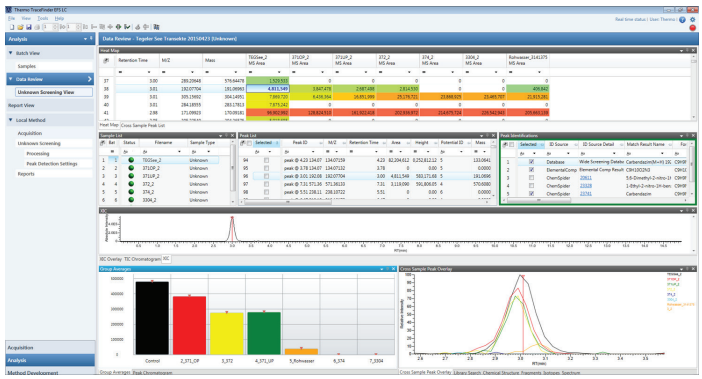
aerobical degradation ($NO_3^-$ -reducing),as for:
- amisulpride
- clindamycin
- metoprolol
- venlafaxine

anaerobical degradation (Mn-reducing), as for:
- candesartan
- carbamazepine
- sucralose

persistent, as for:
- gabapentin
- primidone
- valsartan acid

The third group identified as the critical one, where the components barely show any degradation, so the concentrations found in the sample from the ground water well were still comparable to the ones in the surface water. A total number of 31 components still was detected in the ground water well, with 11 components exceeding a concentration of 0.1 µg/L.

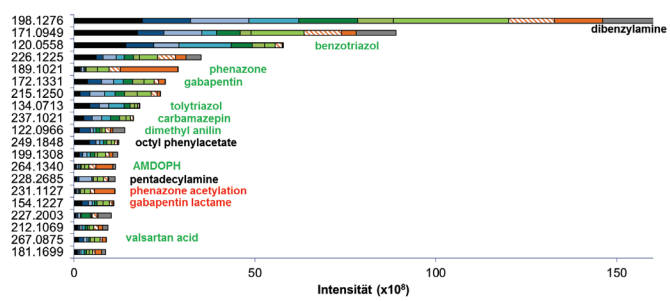
**FIGURE 6. Unknown screening result pane in TraceFinder software, showing the trend analysis of found components and result confirmation.**



### Unknown Screening

In addition to the suspect screening and quantitative analysis, an unknown screening with unbiased peak detection was carried out to screen for additional compounds of interest that had not come to attention yet. The first approach was to look into the 20 most intense compounds after summing up all signal intensities from the different samples for all detected compounds. Eight of these could be easily identified as suspect components already found in the earlier screening. Additional compounds could be identified which had not been found before. The result of this approach is shown in Figure 7.

**FIGURE 7. Unknown Screening Result: Top 20 components by intensity summed up from all samples. Compounds identified in the earlier suspect screening are shown in green, additional compounds identified in the unknown screening process are shown in black, and compounds also found in the degradation product screening are shown in red.**



### Search for Metabolites / Degradation Products

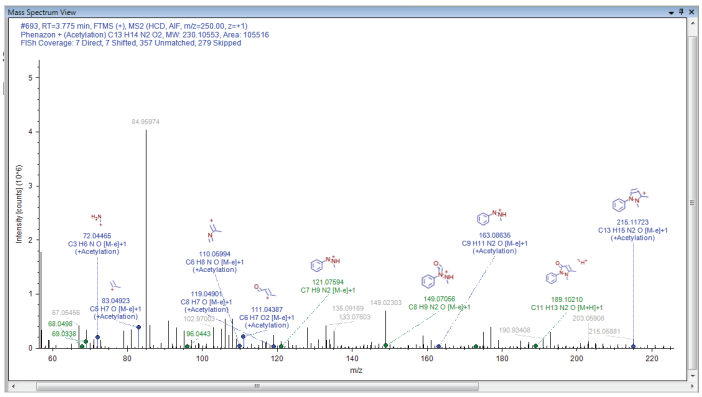
To find out more about the fate of the compounds detected in the process of bank filtration, a search for degradation products was carried out. For this, Compound Discoverer 2.0 software was used.

Compounds already identified during the screening process described above were used as parent compounds and an exhaustive search for degradation products was carried out. In a fully automated process, all possible transformation steps are applied to the given compounds in up to three steps.

As a result, the dehydration of gabapentin was detected, which leads to the gabapentin-lactame, as it is shown already in Figure 6. Also for phenazone the acetylation product could be detected. In addition to the generation of permutations of different transformation steps and generation of the according XICs, the software is able to perform several confirmation steps for the suspected transformation products. The first is an isotopic pattern match of the signals found in comparison with the theoretical pattern derived from the elemental composition of the supposed degradation products. The second is a process called **F**ragment **I**on **S**earc**h** (FISh). Since the data was acquired using the vDIA scan mode, which creates all fragments possible in a data independent approach, all fragments are present all the time.

Figure 8 shows the result of the suspect confirmation by FISh. Due to the vDIA scan mode, where all precursors present in a given mass range, many more fragments are present than only the ones of the suspected compound. Since the fragment data is acquired with high resolution and high mass accuracy, the FISh process can easily pick the fragments belonging to the suspected transformation product and annotate them, resulting in an unambiguous confirmation of the suspected compound.

**FIGURE 8. Unambiguous identification of the phenazone acetylation through HRAM full scan detection and comparison of MS2 data with *in silico* fragmentation data and FISh scoring.**




## Conclusion

In this study, we could show that bank filtration is an important way to reuse surface water that is influenced by effluents from municipal and industrial waste water treatment plants. A wide range of contaminants found in the according surface water is degraded aerobically or anaerobically, although a number of contaminants turned out to be persistent, which still makes it necessary to carry out additional steps of water purification for drinking water generation. The screening and quantitation process described here, using liquid chromatography coupled to high resolution accurate mass spectrometry (LC-HRMS) is a versatile method to quickly assess the quality of the surface water going into the reuse process as well as the raw water used for drinking water generation. It minimizes the analytical effort needed and combines every day routine analyses with extended risk assessment in an easy to handle process.

## References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2. Wode et al. *JCA* **2012**, *1270*, 118–126.
3. Wode et al. *Water Res.* **2014**, *69* (2015), 274–283.
4. Massmann et al. *Hydrol. Processes* **2008**, *22*, 788–801.


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