NATURAL AND ANTRHOPOGENIC ORGANIC MATTER IN THE ISAR RIVER, BAVARIA-GERMANY

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ABSTRACT

The Isar River is one of the most important rivers in South Germany and is the receiver of many WWTP effluents, including Munich. In 2015 a monitoring project started with monthly samplings in 13 different points along the German part of the Isar River. Aim of this project is to identify the organic matter of the surface water, clarify its origins, and how human activities add in the river's pollution along its way.

Samples are analyzed by HILIC-RPLC/API-MS in order to detect the various polar and unpolar organic compounds. All sample results are being compared to the STOFF-IDENT database (non- and suspected target screening) (1). Aim of this database is to gradually be filled with information about compounds that are of interest and can be found in surface water bodies. Additionally, the identified components of the organic matter of the river will be classified according to its origins.

The sampling of the Isar River takes place monthly; starting from the point Isar enters Germany from Austria. The sample points were chosen in a way that will show how the river is affected by the different WWTPs that discharge in its water. Also, one sample is taken from a pristine water source in order to identify which organic compounds in the water have a natural origin, as it has not been affected by anthropogenic activities.

Along with the HILIC-RPLC/API-MS analysis, general chemical parameters of the water samples are measured like DOC, COD and the concentration of certain cations and anions. UV and excitation-emission measurements also take place. The aim of these additional measurements is to obtain a clear view of how these parameters change along the river and seasonally as well as to obtain a thumbprint of the NOM and of the river water's properties.

Keywords: Natural organic matter, anthropogenic contaminants, HILIC-RPLC/API-MS, non-target screening, Stoff-IDENT

1. Introduction
Isar River is the fourth largest river in Bavaria, South Germany, with a total length of 295 km. The springs are in the Karwendel Range of the Alps in Tyrol, Austria and it enters Germany near Mittenwald, and flows through Bad Tölz, Munich, and Landshut before reaching the Danube. Isar is the main receiver of effluent from many waste water treatment plants (WWTP), including Munich.

The monitoring project of the Isar River aims to to identify the organic matter of the river's water, clarify its origins (i.e. natural or anthropogenic), and how human activities add in the river's pollution along its way, using target and suspected target screening analysis.

2. Isar sampling
In 2015 a monitoring project started with monthly samplings in 10 different points along the German part of the Isar River, starting from the Austrian-German borders (Fig 1). Also 3 samples were collected from 3 tributaries of Isar; Seinsbach, Jachen and Loisach. The first one was sampled as a pristine water source, since there is no anthropogenic influence before it

enters in Isar. On the other hand, the other two are both rivers that are affected by anthropogenic activities, such as WWTPs and power plants.
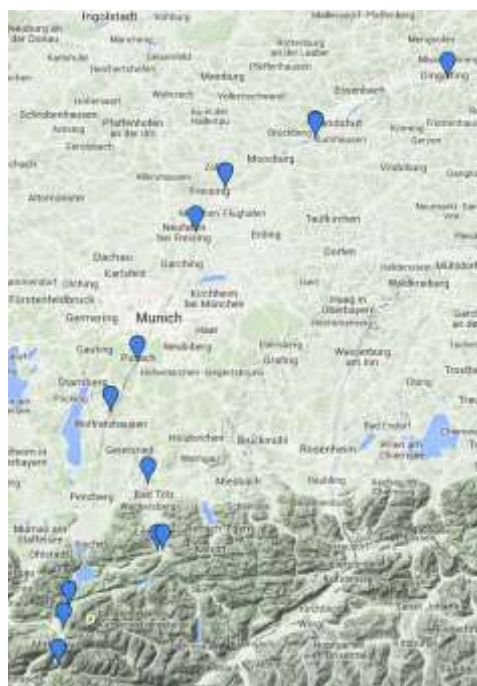

Figure 1: The 13 sampling points of the project along the Isar River.

3.   Sample analysis
3.1. Pretreatment and Preconcentration
All the samples were filtered on the sampling site and collected into brown glass bottles. Until processing time the samples were kept cooled at 4°C. For the preconcentration step three methods were tested; HILIC-RP-SPE, Lyophilise and Parallel Evaporation under vacuum. The method to be chosen must be efficient in preserving compounds from polar to unpolar region, fast and repeatable.

3.2. Physicochemical measurements
Except the trace organics screening, some physico-chemical data was also collected in order to have a complete view of the Isar condition. During the sampling pH, conductivity and dissolved O_2 was measured on site. In laboratory, other measurements which were conducted for are Dissolved Organic Carbon (DOC), Chemical Oxygen Demand (DOC), Total Nitrogen (TN), Cations (Ca^{2+}, Mg^{2+}, K^+, Na^+, NH_4^+), Anions (SO_4^{2-}, Cl^-, NO_3^-, F^-, PO_4^{3-}, HCO_3^-) and Fluorescence Excitation-Emission.

3.3. Trace Organics Screening by HILIC-RPLC/API-MS
The river samples were analysed by HILIC-RPLC/API-MS in order to detect the various trace organic compounds, ranging from polar to unpolar. The Hydrophilic Interaction Liquid Chromatography (HILIC) and Reversed Phase – High Performance Liquid Chromatography (RPLC) are complementary techniques in the separation of organic molecules. Since several years, the young HILIC is a fast-paced technology and allows a systematic separation of very polar compounds which are not retained on typical RPLC stationary phases, and vice versa. The coupling of these two highly orthogonal techniques is nowadays recognized as a useful strategy for the analytical screening of real samples, comprising solutes with a huge variability in their structures and polarities (2-4). An additional advantage is represented by the use in both separation modes of volatile and water miscible solvents (e.g. ammonium acetate aqueous solution and acetonitrile), so that a hyphenation with atmospheric pressure ionization (API) and mass spectrometry (MS) leads to a unique tool for sample screening.

4. Target screening and suspected target screening

4.1. Target Screening

Samples were screened for more than 200 compounds from different polarities and in both positive and negative ionisation mode. Using the exact mass and the normalized retention time of the standards the target screening results were obtained.

4.2. Suspected Target Screening

Suspected Target Screening was realised with the help of the STOFF-IDENT database. For polar compounds (0>logD) the extracted exact masses from the HILIC region of the obtained chromatogram were inserted in the database. The returned results were then filtered and any suggested compounds with a positive logD were rejected.

For the compounds with a positive logD the results were obtained from the database by not only using the exact mass, but also a Retention Time Index (RTI), which takes advantage of the known retention time and logD correlation in RP chromatography, giving much more probable results.

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