Transformation of Micropollutants in the Hyporheic Zone

Malte Posselt

Academic dissertation for the Degree of Doctor of Philosophy in Applied Environmental Science at Stockholm University to be publicly defended on Monday 27 April 2020 at 10.00 in De Geersalen, Geovetenskapens hus, Svante Arrhenius väg 14.

Abstract

Hyporheic zones (HZs) are reactive transition regions between rivers and aquifers which are thought to play an important role in the attenuation of micropollutants. Micropollutants are chemical substances such as pharmaceuticals, industrial chemicals or personal care products that are found in trace concentrations in the environment and that can be harmful to organisms. This thesis aimed to narrow the knowledge gap on the environmental fate of wastewater-derived polar organic micropollutants in the aquatic environment, with a specific emphasis on the hyporheic zone.

In **Paper I** an efficient workflow was developed for the in-situ characterization of polar organic micropollutants and their transformation products (TPs) in the hyporheic zone at high spatial and temporal resolution and with minimal disturbance of natural flow paths. A low volume sampling device was combined with a newly developed high throughput-direct injection-UHPLC-MS/MS method. Application in the field revealed significant differences in micropollutant concentrations that varied over small time- and spatial scales. In **Paper II** the results of a comprehensive field study performed in the urban lowland river Erpe in Berlin, Germany, are presented. The work provided data on in-situ attenuation behavior of 24 micropollutants and TPs, along with novel insights into the spatially- and temporally varying environmental factors which play a major role in controlling in-stream attenuation of micropollutants. **Paper III** describes a novel, multi-flume experiment designed to investigate the influence of hyporheic exchange flow and sediment bacterial diversity on dissipation half-lives of 31 micropollutants and associated TPs. Attenuation and transformation of most substances increased significantly with bacterial diversity; fewer compounds responded to both bacterial diversity and hyporheic exchange flow. In addition to the discovery of several novel TPs, a number of bacterial strains were identified that might be associated with micropollutant degradation. In **Paper IV** the fate of metformin in the hyporheic zone was examined using large-scale (100m) recirculating flumes to perform realistic yet well-controlled experiments. In addition to determining dissipation half-lives in surface and pore water, the formation of novel TPs was investigated via suspect screening and bacterial communities were characterized using microbiological analyses. Data from these experiments indicate that dunes and macrophytes promote hyporheic exchange flow and create reactive environments with steep and varying biogeochemical gradients, which enhanced the degradation of metformin.

Collectively, the fate of 33 parent compounds and 37 transformation products was assessed in field and mesocosm experiments described in this thesis. Additionally, 29 suspected TPs were tentatively identified. Higher bacterial diversity in the hyporheic zone and more intense hyporheic exchange flows significantly enhanced biodegradation of organic micropollutants. A number of known and novel TPs were discovered under diverse conditions, many of which showed signs of environmental persistence, providing further evidence for inclusion of TPs in contaminant risk assessments and regulatory frameworks. This work highlights the importance of considering both small- and reach-scale temporal and spatial variability for a mechanistic understanding of attenuation in in-stream studies.

Keywords: *micropollutants, hyporheic zone, biodegradation, bacteria, pharmaceuticals, transformation products, LC-MS/MS, macrophytes, bedforms, suspect screening, mesocosm, flume, river.*

Stockholm 2020
http://urn.kb.se/resolve?urn=urn:nbn:se:su:diva-179883

ISBN 978-91-7911-038-3
ISBN 978-91-7911-039-0

Department of Environmental Science

Stockholm University, 106 91 Stockholm