Report by UWI doctoral researcher Jonas Schaper (N6)

Project number: N6

First and last name of doctoral researcher: **Jonas L. Schaper**

(Working) title of doctoral project: **Retention of trace organic compounds in hyporheic reactors of urban freshwater systems**

Name of supervisors: Dr. Jörg Lewandowski (IGB), Dr. Anke Putschew (TUB), Prof. Dr. Gunnar Nützmann (IGB)

2. Description of doctoral project and research results achieved to date:

Motivation, Aims and Hypothesis

Trace organic compounds (TrOCs) are frequently detected in urban surface waters in which they impair ecosystem health and pose risks for drinking water production [1,2]. In lotic systems, surface water is continuously exchanged with saturated streambed sediments, i.e. the hyporheic zone (HZ). The HZ is characterized by steep biogeochemical gradients, divers microbial communities and relatively high microbial turnover rates [3,4]. It was therefore suggested that along hyporheic flow paths, TrOCs can be efficiently removed [5]. If so, the HZ might (i) act as a reactive barrier protecting groundwater from surface water and vice versa and (ii) contribute to overall removal of TrOCs in rivers on the reach scale. River restoration measures that aim at increasing hyporheic exchange fluxes would thus promote water quality in urban rivers. However, quantitative information on the in-situ fate of TrOCs in the HZ (e.g. first-order removal rate constants) was largely non-existing in the scientific literature. Furthermore, the influence of biogeochemical and physical factors, such as redox conditions or temperature, on removal rate constants of TrOCs in the HZ was largely unknown. As a consequence, the relative contribution of the HZ to reach-scale, in-stream removal of TrOCs, that is the relative importance of the HZ with respect to self-purification processes in rivers has not been quantified.
The main aims of the present dissertation are therefore (i) providing in-situ first-order removal rate constants for several TrOCs in the HZ of urban streams, (ii) determine the hydrological, physical and biogeochemical factors that limit the efficiency of the HZ in removing TrOCs and, (iii) quantify the relative contribution of hyporheic removal to in-stream (i.e. surface water, reach-scale) removal of TrOCs. It was hypothesized that in urban rivers removal rate constants in the HZ substantially deviate from rates obtained in laboratory studies and bank filtration systems. As reaction rates for many TrOCs are likely to be redox-dependent, removal efficiency is expected to be strongly controlled by redox conditions in the HZ. As a consequence, it was hypothesized that in first-order, urban streams the fate of many TrOCs will be largely controlled by their respective reactivity (i.e. removal rate constants) in the HZ and by the intensity of hyporheic exchange fluxes.

Current State of Work

The main part of the dissertation work can be structured in three parts, each constituting a research article. The first part (paper I, Schaper et al., 2018) reports the findings of a field experiment carried out at River Erpe, Berlin, an urban lowland river that receives 70-80% of its streamflow from a large municipal wastewater treatment plant (WWTP). The study investigates the fate of several TrOCs that enter the HZ at a river section, where downwelling conditions prevail. A simple, 1D advection-dispersion transport model is used to calculate first-order removal rate constants from equilibrium depth profiles, sampled in the HZ using porewater peepers [6]. While some TrOCs (such as carbamazepine) are relatively stable along the investigated hyporheic flow paths (~20 cm), others (such as acesulfame, gabapentin, benzotriazole) are readily attenuated in the HZ (Figure 1). For some compounds, removal rate constants are not influenced by ambient redox conditions (e.g. diatrizoic acid). For the majority of TrOCs investigated, however, removal is insignificant in anoxic (e.g. iron and manganese reducing) sections of the HZ. Under oxic to suboxic (i.e. denitrifying) conditions, half-lives of many TrOCs are relatively low (several hours). The study concludes that the HZ is efficiently removing many TrOCs, although removal is strongly influenced by redox conditions.

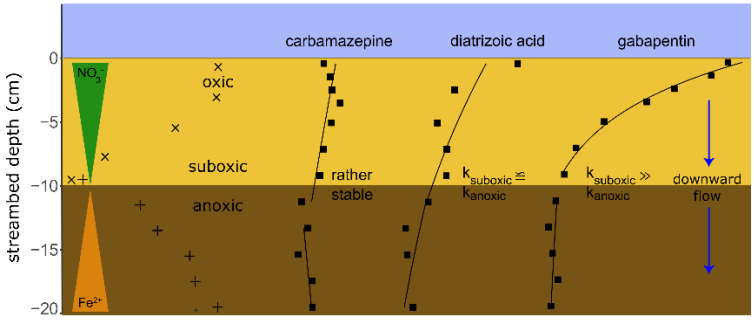

Figure 1: Graphical abstract of paper I showing the redox zonation in the HZ and concentration depth profiles of three TrOCs. While some TrOCs, (e.g. carbamazepine) are found to be rather stable in the HZ, others such as diatrizoic acid and gabapentin are well removed along hyporheic flow paths (adapted from Schaper et al. (2018), Water Research).

The second part of the dissertation (paper III) also reports findings from a field experiment conducted at River Erpe. Here, concertation time series of TrOCs in hyporheic porewater, collected via an active porewater sampling method, are evaluated using a numerical, transient 1D advection-dispersion model. The aim of this study was to calculate removal rate constants of TrOCs and many of their transformation products (TPs) in the HZ under different seasonal conditions and to evaluate the importance of retardation of TrOCs along hyporheic flow paths. To this end porewater in the HZ was sampled hourly for 32 h at four different depths both under winter (early April) and summer (June) conditions. The experiment was conducted in collaboration with doctoral researcher M. Posselt (University of Stockholm, Sweden) and UWI Kollegiate A. Jäger in the framework of a large joint field experiment carried out by doctoral students of the HypoTrain ITN in 2016. Currently, data evaluation is in progress (planned submission date of paper III: 01.08.2018). A second publication on the active sampling method and a novel LC-MS/MS protocol developed by M. Posselt at Stockholm University was recently submitted.

The third part of the dissertation investigates the overall significance of the HZ with respect to reach-scale removal of TrOCs in small, urban rivers. The relative contribution of the HZ to reach-scale, in-stream removal is not only a function of the hyporheic reactivity of TrOCs but also depends on the intensity of exchange fluxes between the surface water and the HZ. Two tracer experiments were conducted in both dry and wet seasons along a 3 km reach of a first-order stream in the Adelaide Hills, Australia that receives discharge from a small WWTP. Breakthrough curves were evaluated using a transient model to characterize seasonal differences in stream residence time and transient storage. Simultaneously, Lagrangian and time-integrated surface water sampling were conducted to calculate half-lives of TrOCs in the surface water. Half-lives in the HZ were calculated using porewater samples obtained from a modified mini-point sampler and hyporheic residence times measured via active heat-pulse sensing. Using the modelled transport parameters, it was subsequently estimated that during the wet season removal in the HZ was the main driver for in-stream removal of TrOCs in the investigated river reach (Figure 2).

The outcome of this dissertation strongly suggests, that the HZ is able to significantly remove many TrOCs on relatively short (cm) flow paths. If hyporheic exchange is important on the reach scale, it is shown that the HZ is the main driver for in-stream removal of TrOCs. It is therefore suggested that river restoration measures, aiming at increasing hyporheic exchange will improve reach-scale, in-stream TrOCs removal and hence water quality in urban streams.

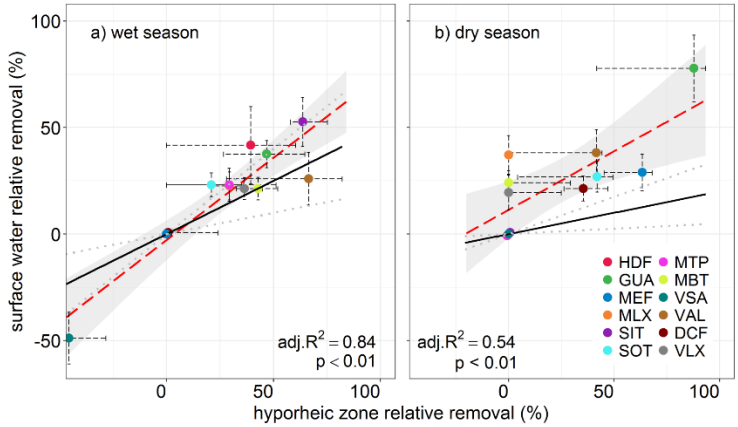

Figure 2: Correlation (red dashed line and associated 95% confidence interval in grey) between the median hyporheic relative removal (%) and the reach-scale relative removal between Site A and Site B during the wet season (a) and the dry season (b). The black line represents a theoretical mixing line with a slope of L_c/L_s that depicts the predicted in-stream removal (%) given a relative removal in the HZ after a mean residence time in the transient storage zone of τ_{hz}. Adapted from Schaper et al. (2018).

Future Work planned

Experimental results of paper III (the second part of the dissertation) are currently evaluated (planned submission August 2018). An additional experiment was conducted to evaluate the fate of TrOCs during river bank filtration at a study site at River Erpe.

Collaboration

The research project is part of the common topic groups “groundwater-surface water interactions“ and “modeling“. A strong collaboration was established with the University of Stockholm and the HypoTRAIN ITN. M. Posselt (Department of Environmental Science and Analytical Chemistry (ACES), Stockholm University) contributed with his novel analytical procedure to measure transformation products of many TrOCs. The data provided by M. Posselt complemented the analytical protocol established previously at the Chair of Water Quality Engineering, TUB (formerly Water Quality Control). Further intense collaboration was

established with researches (M. Shanafield, E. Banks, J. McCallum and Okke Batelaan) from Flinders University, Adelaide Australia.

References

1. Pal, A., He, Y., Jekel, M., Reinhard, M., Gin, K. Y. H. (2014): Emerging Contaminants of Public Health Significance as Water Quality Indicator Compounds in the Urban Water Cycle. *Environ. Int.*, *71*, 46–62
2. Schwarzenbach, R. P., Escher, B. I., Fenner, K., Hofstetter, T. B., Johnson, C. A., Von Gunten, U., Wehrli, B. (2006): The Challenge of Micropollutants in Aquatic Systems. *Science (80-.).*, *313* (5790), 1072–1077
3. Boano, F., Harvey, J. W., Marion, A., Packman, A. I., Revelli, R., Ridolfi, R., Wörman, A. (2014): Hyporheic Flow and Transport Processes: Mechanisms, Models, and Bioghemical Implications. *Rev. Geophys.*, 1–77
4. Krause, S., Lewandowski, J., Grimm, N. B., HA.h, D. M., Pinay, G., McDonald, K., Martí, E., Argerich, A., Pfister, L., Klaus, J., et al. Ecohydrological Interfaces as Hot Spots of Ecosystem Processes. *Water Resour. Res.* 2017, *53* (8), 6359–6376
5. Lewandowski, J., Putschew, A., Schwesig, D., Neumann, C., Radke, M. (2011): Fate of Organic Micropollutants in the Hyporheic Zone of a Eutrophic Lowland Stream: Results of a Preliminary Field Study. *Sci. Total Environ.*, *409* (10), 1824–1835
6. Hesslein, R. H. (1976): An in Situ Sampler for Close Interval Pore Water Studies. *Limnol. Oceanogr.*, *21* (6), 912–914

3. Comments on the qualification programme and supervision strategy:

I personally think that by putting a 3 year constrain on a PhD thesis, the DFG restricts personal and professional development of PhD students. I suggest adjusting the schedule to a 3+1 system as it is typically implemented in the Scandinavian countries and in Switzerland. The supervision strategy completely met my expectations. In particular I value the high degree of scientific freedom and that I was given the opportunity to be mobile and to collaborate with different working groups. However, I strongly argue to make CO_2 compensation for travel of all scientific staff involved in the RTG mandatory and include extra funding for this purpose.

Participation in the following Research Training Group events (internal and external):

1. Core courses
   - I – Urban interface processes – fluxes, transport, interactions (3 ECTS)
   - II – Modelling and measuring concepts of interface processes (3 ECTS)
   - III – Urban freshwater ecology (3 ECTS)
2. Elective courses
   - Oral and poster presentation (IGB Berlin, 23.11.2015 - 24.11.2015)
   - Proposal writing
3. Gender courses
   - none offered for males
4. Other UWI events
   - UWI Opening Ceremony (08. - 09.09.2015)
   - Exposé Talks (08.12.2015)
   - Summer School (13. - 14.09.2016)
   - Interim Meeting (19.05.2017)
   - Summer School (18.-20.09.2018)
5. HypoTRAIN ITN courses, Advanced Training Courses (ATCs)
   - ATC 1: HypoBasics (22. - 26.06.2015, 3 ECTS)
   - ATC 2: Sampling in hyporheic zones, in situ measurement techniques & Designing experiments in the hyporheic zone (02. - 06.11.2015, 3 ECTS)
   - ATC 3: Modeling Hyporheic Processes (28. - 30.10.2015, 2 ECTS)
   - ATC 4: Organic Pollutants in aquatic systems (29.02 - 01.03.2016, 1 ECTS)
6. IGB Courses
   - Scientific Writing by T. Mehner (05. - 09.12.2016, 3 ECTS), paper I was to a large extent written during this course

Research stays or internships at other research institutions both at home and abroad: Multiple stays at Flinders University, South Australia (∑~ 1a). Research visit at University of Stockholm, Sweden (3 weeks, October 2016).

Participation in conferences, congresses, etc., at home and abroad:

2015:

- Goldschmidt Conference (16. - 21.08.2015, Prague, Czech Republic)
- 17th IWA International Conference on Diffuse Pollution and Eutrophication (13. - 17.09.2015, Berlin, Germany)

2016:

- AGU Fall Meeting (12. - 16.12.2016, San Francisco, USA)

2017:

- HydroEco Conference, (28. - 31.03.2017, Birmingham, United Kingdom)

2018:

- EGU General Assembly (08. - 13.03.2018, Vienna, Austria)

4. Individual publications:

I. Articles:

- Schaper,J.L., Seher,W., Nützmann,G., Putschew,A., Jekel,M., & Lewandowski,J. (2018). The fate of polar trace organic compounds in the hyporheic zone. Water Research, 140, 158-166
- Schaper,J.L., Posselt,M., McCallum,J.L., Banks,E.W., Hoehne,A., Meinikmann,K., Shanafield,M.A., Batelaan,O. & Lewandowski,J. (2018): Hyporheic exchange controls fate of trace organic compounds in an urban stream. *Environmental Science & Technology,* 52, 12285-12294
- Posselt,M., Jaeger,A., Schaper,J.L., Radke,M., & Benskin,J.P. (2018): Determination of polar organic micropollutants in surface and pore water by high-resolution sampling-direct injection-ultra high performance liquid chromatography-tandem mass spectrometry. *Environmental Science: Processes & Impacts*, accepted

II. Conference, poster presentations etc.:

- Jäger,A., Posselt,M., Schaper,J. and Lewandowski,J. (2017): Attenuation of organic micropollutants in an urban lowland stream under varying seasonal and hydrological conditions. Vienna, EGU General Assembly, 23 Apr. – 28 Apr. 2017, poster
- Jäger,A., Posselt,M., Schaper,J., Riml,J. and Lewandowski,J. (2017): Using intrinsic diurnal concentration fluctuations in an urban lowland stream to simulate transport and fate of organic micropollutants with the the one-dimensional transport model OTIS. Birmingham, HydroEco, 18 Jun. – 23 Jun. 2017, poster
- Jäger,A., Posselt,M., Schaper,J., Betterle,A. and Lewandowski,J. (2018): Self-purification capacity of an urban lowland stream - an attempt to identify drivers for in-stream transformation processes of organic micropollutants. Vienna, EGU General Assembly, 8 Apr. – 13 Apr. 2018, PICO presentation
- Jäger,A., Posselt,M., Schaper,J. and Lewandowski,J. (2017): Formation of transformation products from wastewater-derived pharmaceuticals in an urban lowland stream. New Orleans, AGU fall meeting, 11 Dec. – 15 Dec. 2017, poster
- McCallum,J., Shanafield,M.A., Banks,E.W., Schaper,J.L., Meinikmann,K., Höhne,A., Batelaan,Okke and Lewandowski,J. (2017): Seasonal dynamics of residence times in a perennial, wastewater impacted stream. Sydney, Australasian Groundwater Conference , 11 Jul. – 13 Jul. 2017, poster
- Schaper,J.L., Seher,W., Nützmann,G., Putschew,A., Jekel,M. and Lewandowski,J. (2018): Fate of polar trace organic compounds in the hyporheic zone. Vienna, EGU General Assembly, 8 Apr. – 13 Apr. 2018, PICO presentation
- Schaper,J.L., Posselt,M., Shanafield,M.A., Banks,E.W., Höhne,A., Meinikmann,K., Putschew,A. and Lewandowski,J. (2018): Fate of trace organics and their metabolites in an urban stream in South Australia. Vienna, EGU General Assembly, 8 Apr. – 13 Apr. 2018, PICO presentation
- Schaper,J.L., Höhne,A., Meinikmann,K., Shanafield,M.A., Banks,E.W., McCallum,J., Posselt,M., Putschew,A., Nützmann,G., Batelaan,Okke and Lewandowski,J. (2017): Relative contribution of hyporheic to whole stream attenuation of trace organics in an urban stream. Birmingham, HydroEco, 18 Jun. – 23 Jun. 2017, poster
- Schaper,J.L., Popp,A.L., Meinikmann,K., Shanafield,M.A., Banks,E.W., Putschew,A., Nützmann,G. and Lewandowski,J. (2016): Fate of polar organic trace compounds infiltrating into an alluvial aquifer from an urban lowland river. San Francisco, AGU fall meeting, 12 – 16 Dec. 2016, talk
- Shanafield,M.A., Banks,E.W., Schaper,J.L., Meinikmann,K., Höhne,A., Batelaan,Okke and Lewandowski,J. (2017): Groundwater-surface water interactions in metropolitan areas - a DAAD scheme collaboration between Flinders University & Leibniz-Institute of Freshwater Ecology and Inland Fisheries (IGB). Canberra, Universities Australia Higher Education Conference, 1 Mar. – 3 Mar. 2017, poster
- Posselt,M., Schaper,J., Ribbenstedt,A. & Benskin,J.P. (2016): Fingerprinting micropollutant transformation in hyporheic zones. Nantes, SETAC Europe 26th Annual Meeting, 22 – 26 Jun. 2016, poster
- Posselt,M., Schaper,J. & Jäger,A. (2016): Investigating time series depth profiles of micropollutants in hyporheic zones. Berlin, EHF (European Hyporheic Forum), 13 Jun. 2016, poster