Marie Skłodowska-Curie

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"HypoTRAIN"

Hyporheic Zone Processes – A training network for enhancing the understanding of complex physical, chemical and biological process interactions

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Deliverable D3.1

Validated methods for passive sampling micropollutants and measuring transformation rates

Dissemination Level of Deliverable:

PU	Public	**X**
CO	Confidential, only for the members of the consortium (including the Commission Services)	
CI	Classified, as referred to in Commission Decision 2001/844/EC	

Contents

Validated methods for passive sampling micropollutants and measuring transformation rates

WP3: Micropollutant Transformation and Fate

WP Leaders: Anna Sobek and Jonathan Benskin

ESRs 1 (SU-Posselt/Benskin), 7 (IWW-Raza/Schueth), 14 (Eawag-Meschelke/Hollender)

1. Summary

Deliverable 3.1 lays the groundwork for WP3 'Micropollutant Transformation and Fate', which seeks to generate new quantitative information on the dependence of the attenuation of organic micropollutants on biogeochemical and hydraulic constraints and on the role of the hyporheic zone in self-purification.
Development of passive sampling methodology was carried out by ESR 3 (Jonas Meschelke, supervisor: Juliane Hollender; Eawag). A novel passive sampler was developed which utilizes an Empore™ SDB-RPS extraction disc (binding phase) covered by an agarose diffusion layer and a polyethersulfone membrane filter housed in a steel holder. Several individual samplers are affixed along a bar which is then submerged into the sediment, so that some samplers are above the sediment, and others are below the surface of the sediment. Validation experiments were performed using tap water spiked with 192 micropollutants at a concentration of 600ng/L in both a circular flume and stagnant water. The samplers were exposed for 14 days, then extracted and analyzed by LC-MS/MS. Initial results indicate significant, yet flow rate-insensitive uptake of micropollutants onto the passive sampler. The device was subsequently deployed in the joint field sampling campaign on the Erpe river in June, 2016.
Development of a method for determination of in situ transformation methods was carried out by ESR 1 (Malte Posselt, supervisor: Jonathan Benskin; SU). The overall goal of this work was to use minimally-invasive high resolution time series sampling, combined with electric conductivity data (for determination of pore water flow velocity) and a sensitive UHPLC-MS/MS method in order to improve accuracy of determination of environmental contaminant transformation rate constants compared to lab-based experiments. A suite of model compounds and transformation products were selected based on environmental relevance (production volumes, toxicity and persistence) and prior biodegradation experiments, which cover a wide range of physical–chemical properties. A new, minimally invasive, semi-automated pore water sampling instrument was developed and tested together with Jonas Schaper (IGB). The device modifies and improves upon the USGS MINIPOINT sampler. Each minipoint sampler consists of a 1.5 m steel tube (3 mm outer diameter) which is perforated at the tip allowing water passage but keeping sediment particles out. Water samples are collected automatically with syringe pumps using syringes which are coupled to the sampler with PEEK tubing. The minipoint samplers are used in combination with high resolution electric conductivity (EC) measurements, obtained using CTD divers which are fixed to the tip of stainless steel tubes. One of these 'EC-lances' is placed with its sensor 10 cm downstream and at the same sediment depth to each of the minipoint samplers. This approach ensures that pore water flow around the minipoint samplers is not disturbed while flow velocity is expected to be similar. The instrumentation is used at a location where downwelling conditions (pore water flow from

surface water to groundwater). The diurnal fluctuation of EC (which occurs due to an effluent water pulse from the local WWTP) is employed to estimate pore water travel time during hyporheic zone passage (Schwientek et al. 2016). In downwelling zones the direction of flow is expected to be predominantly mono-directional from surface to groundwater. Conservative tracers (Acesulfam, Carbamazepine) are used to correct for dilution effects. Instrumental analysis was carried out using a novel UHPLC-MS/MS method. Validation of the procedure was carried out using a suite of laboratory and field trials, as well as spike/recovery experiments involving pore water, surface water, and effluent.

The contribution of biodegradation to overall micropollutant attenuation in a river system requires knowledge of pollutant sorption behavior and factor(s) influencing this behavior. Consequently, ESR 7 (Muhammad Raza, supervisor Christoph Schueth; IWW) focused on development of a procedure for studying sorption of micropollutants in the hyporheic zone. The method involves mixing air-dried soil samples with river water in various proportions and the incubating them with various concentrations of the model compound diclofenac. The experiments were performed for 48hrs at room temperature after which samples were collected. The samples were extracted by SPE and then reduced in volume and derivatized, prior to analysis by GC-MS.

2. Passive sampling method used within the HypoTRAIN project

Jonas Mechelke[1,2], Etiënne L.M. Vermeirssen[3], Juliane Hollender[1,2]

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a. Aim of the method/desired application

- Monitoring time-weighted average concentrations of polar and semi-polar organic pollutants at low flow velocities (10^{-5} to 0.01 m/s), as encountered in groundwater or hyporheic zones
- Enrichment of transformation products in situ (increased stability due to sequestration by the passive sampler binding phase)

b. Brief description

- Passive sampler design inspired by polar Chemcatcher® and o-DGT passive samplers (Fig. 1 and 2):
  - Empore™ SDB-RPS extraction disc (binding phase) covered by an agarose diffusion layer and a polyethersulfone membrane filter
  - Assembly in a stainless steel housing

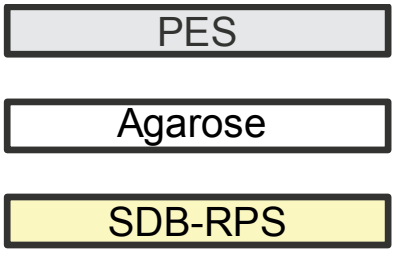

Figure 1. *Schematic design of the passive sampler. An extraction disk (lower layer, SDB-RPS) is covered by an agarose diffusion layer (middle) and a p polyethersulfone (PES) membrane filter (upper layer).*

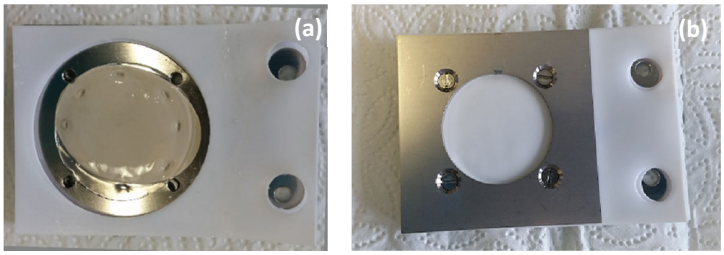

Figure 2. *An extraction disk (SDB-RPS in Fig. 1) covered with an agarose diffusion layer (a) and a polyethersulfone membrane filter (PES in Fig. 1) are assembled to be employed as a passive sampler for organic micropollutants.*

- Field installation:
  - Fixation of assembled passive samplers on passive sampler holder bar (Fig. 3)
  - Positioning of passive samplers (holder bar) in water column above the sediment surface and at desired sediment depths using a specifically developed installation kit (Fig. 4)
  - Exposure for 10 to 20 days depending on flow and concentration level

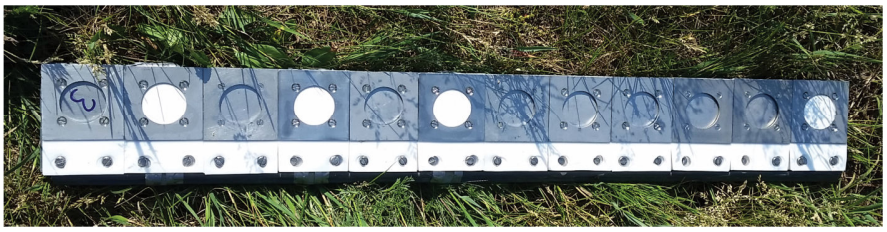

Figure 3. *A row of passive samplers fixed on a holder bar, ready for installation in river water and hyporheic sediments.*

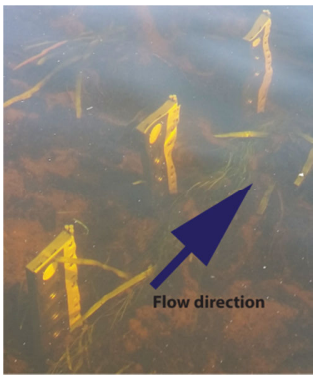

Figure 4. *Passive samplers installed in flowing water and hyporheic sediments.*

c. Method validation

- Step 1:
  - In a first experimental approach, pollutant uptake by four different passive samplers that feature a design similar to those of polar Chemcatcher® and o-DGT samplers, was evaluated in a circular flume (Fig. 4) and in stagnant water (Fig. 5). 192 pollutants, i.e. mostly polar (log D_{pH8} -4.6 to 5.3) pharmaceuticals and related transformation products, were spiked into tap water at a concentration of 600 ng/L. Passive samplers were exposed for 14 days, extracted and the extracts analyzed by liquid chromatography-high resolution mass spectrometry. First results indicated the best performance, i.e. the most flow rate insensitive but yet significant pollutant uptake, for the abovementioned passive sampler design (SDB-RPS/Agarose/PES, Figures 1 and 2). It was therefore selected for deployment during the JFE in June 2016 at river Erpe in Berlin.

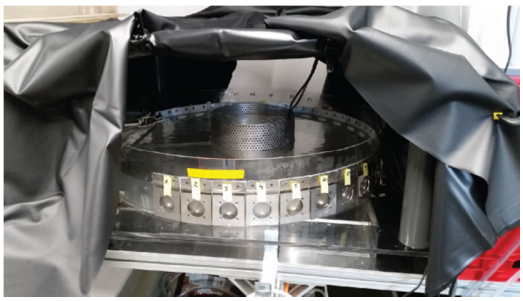

Figure 5. *Circular flume used for method validation.*

Figure 6. *Stagnant water conditions were simulated using an aquarium.*

  - Current status:
    - Experimental part: conducted
    - Data analysis: being finalized

- Step 2:
  - The effect of flow rate (0.03 to 0.4 m/s) on sampler performance will be studied in recirculating flumes
  - Status: open

- Step 3:
  - The effect of flow rate (m/day range) on sampler performance will be studied in recirculating sediment boxes
  - Status: open

d. Publication status

- The work will be published as (a) peer-reviewed article(s).

- Upcoming conference: 8th International Passive Sampling Workshop And Symposium - September, 7.-10. 2016 – Prague, Czech Republic; Poster presentation; Title: “Development of a passive sampler to trace polar organic pollutants at low flow velocities along hyporheic flow paths”

3. Measuring in situ transformation rates of micropollutants in river sediments

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a. Aim

The overall goal of this work is to apply innovative sampling and analysis methods in order to improve characterization of micropollutant behaviour in hyporheic river sediments. We hypothesize that in situ, minimally-invasive high resolution time series sampling, combined with electric conductivity data (for determination of pore water flow velocity) and a sensitive UHPLC-MS/MS-based approach will improve accuracy of determination of environmental contaminant transformation rate constants compared to lab-based experiments.

b. Overview

Model compounds (Table 1) were selected based on environmental relevance (production volumes, toxicity and persistence) and to cover a wide range of physical–chemical properties. Transformation products were selected according to data from bottle incubations (Li et al. 2015). For quantitative analysis of both, parent and transformation products, a sensitive direct-injection UPLC-MS/MS method was developed. Direct injection enables us to sample very small pore water volumes using very thin sampling tubes, without the need for off-line extraction and pre-concentration. These features ensure minimal disturbance of the hyporheic zone during sampling, and prevent surface water infiltration along sampling devices, thereby improving the validity of the acquired data.

c. Sampling techniques

(*Sampling techniques were developed in collaboration with Jonas Schaper, Leibniz-Institute of Freshwater Ecology and Inland Fisheries (IGB), Urban Water Interfaces training group UWI*)

A new, minimally invasive, semi-automated pore water sampling instrument was developed and tested (Figure 7). The device modifies and improves upon the USGS MINIPOINT sampler (Duff et al. 1998). Each minipoint sampler consists of a 1.5 m steel tube (3 mm outer diameter) which is

perforated at the tip (ultrafine laser-cut slits) allowing water passage but keeping most sediment particles out. Tightly fitting PEEK tubing is inserted down to the perforated tip of the steel tube (reducing the dead volume significantly). The other end of the tubing is connected to a plastic 20 ml syringe. The syringes are operated automatically using NE-1600 syringe pumps (New Era Pump Systems, Inc, Farmingdale, USA) and emptied after each sampling event. Collected water samples are then filtered (45 µm, activated cellulose syringe filters) and further processed.

The minipoint samplers are used in combination with high resolution electric conductivity (EC) measurements in the hyporheic zone as follows: EC is measured using CTD divers from Schlumberger Water Services (Willemstad, Curaçao, Kingdom of the Netherlands) which are fixed to the tip of stainless steel tubes of defined length and covered with fine nylon fabric to allow unhindered water exchange while at the same time protecting the sensor from sediment. One of these 'EC-lances' is placed with its sensor 10 cm downstream and at the same sediment depth to each of the minipoint samplers. This approach ensures that pore water flow around the minipoint samplers is not disturbed by the EC lance while flow velocity is expected to be similar at both locations.

The instrumentation is used at a location where downwelling conditions (pore water flow from surface water to groundwater) are expected. This is confirmed using temperature lances (Umwelt- und Ingenieurtechnik GmbH, Dresden, Germany) installed in close proximity to the samplers.

The diurnal fluctuation of electric conductivity which is due to the effluent water pulse from WWTPs is employed to estimate pore water travel time during hyporheic zone passage (Schwientek et al. 2016). In downwelling zones the direction of flow is expected to be predominantly monodirectional from surface to groundwater. Conservative tracers (Acesulfam, Carbamazepine) will be used to correct for dilution effects.

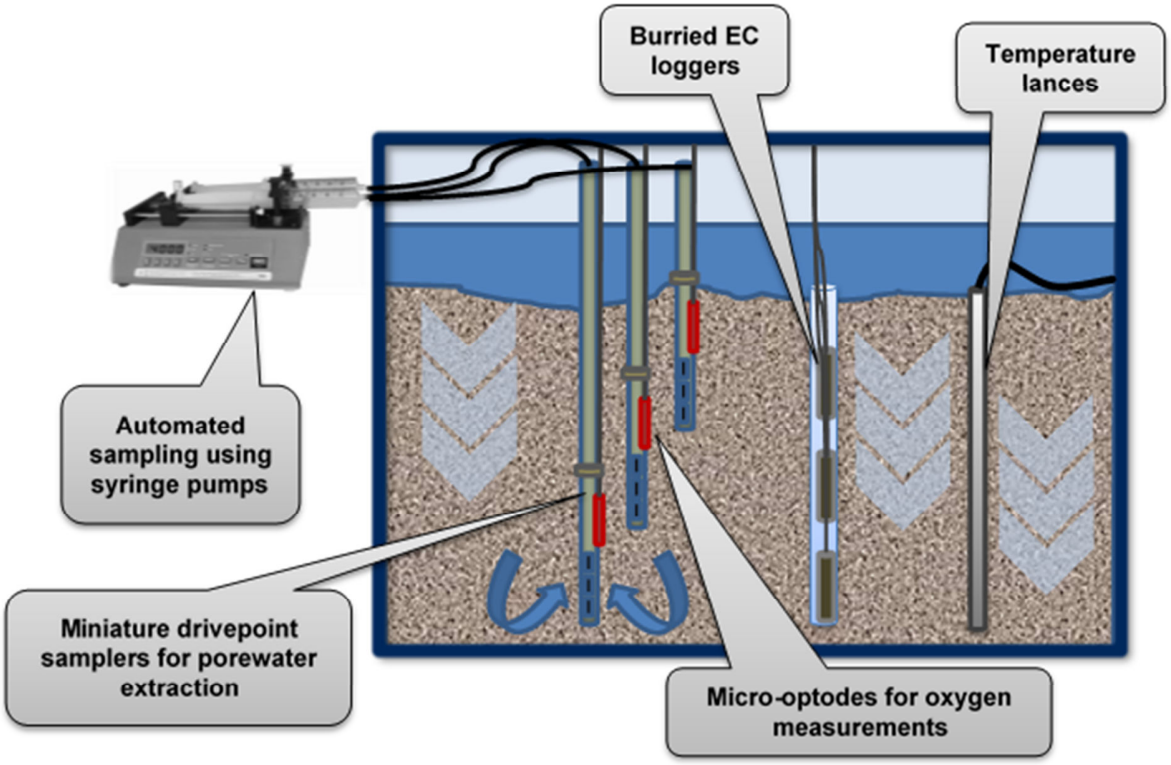

Figure 7. *Illustration of the minipoint sampler set-up.*

d. Instrumental analysis

One fraction of the filtered pore water samples is analyzed for organic micropollutants and transformation products using a newly developed and validated method utilizing ultra-high performance liquid chromatography tandem mass spectrometry (UHPLC-MS/MS).

Isotopically-labelled internal standards (Table 2) were purchased from Toronto Research Chemicals Inc., North York, Canada and Sigma Aldrich, St. Louis, MO, USA. Stock solutions of each test compound and internal standards were prepared in methanol (c = 1 g/L). A working solution containing all internal standards in methanol (c = 5000 µg/L) was prepared. Prior to analysis, 500 µL of each sample are transferred to a HPLC vial, 5 µL of the internal standard working solution are added and the vial is thoroughly mixed using a vortex device.

Separations are carried out on a Thermo Scientific (Waltham, USA) Dionex Ultimate 3000 UHPLC system equipped with a Waters (Manchester, UK) ACQUITY UPLC HSS T3 column (1.8 µm, 2.1 mm x 100 mm). A mobile phase gradient of 100 % deionized water (+10 mM acetic acid) (A) and 100 % methanol (+10 mM acetic acid) (B) is used. The gradient is run from 99 % A to 40 % B in 2.2 min, to 98 % B in 3.3 min, remains at 98 % B for 0.5 min and is then returned to 97 % A for equilibration (3 min). The flow rate is set to 600 µL/min during separation and 1200 µL for equilibration. The column oven temperature is set to 40 °C. For MS/MS analysis a Thermo Scientific (Waltham, USA) Quantiva triple-stage quadrupole mass spectrometer with an H-ESI interface is used.

The mass spectrometer was operated in polarity switching, selected reaction monitoring mode. Individual precursor/product ion transitions are provided in Table 3. Multiple ions for a given target were included and their ratio was used to confirm an absence of interferences.
MS parameters were optimized using standard solutions (1 mg/L) of each analyte which were infused directly into the mass spectrometer. The spray voltage is set to 5.5 kV, the sheath gas to 38 arbitrary units and the auxiliary gas to 10 arbitrary units. The ion transfer tube temperature is set to 305 °C and the vaporizer temperature to 350 °C.
A series of calibration standards containing all target compounds and the internal standards is measured in the beginning, in the middle and in the end of each series of samples. In addition, one standard is measured every 10 samples for quality control.
MS data are processed using the Thermo Scientific (Waltham, USA) Xcalibur 3.1.66.10 instrument software and quantified using the internal standards method.

e. Validation

Validation of the sampling methodology has taken place using:

1. Laboratory trials of minipoint samplers.
2. Field trial (Erpe river) during a Hypotrain secondment in April 2016. Time series sampling over 24 hours was performed with hourly sampling (1 ml/min) in three different sediment depths.
3. Second field trial with improved instrumentation according to the experience gathered in the first field trial. 34 hour time series sampling in four different sediment depths (hourly sampling (1 ml/min)).

Oxygen micro optodes located at the minipoint sampler tips were used to test for surface water infiltration during pore water sampling. This was not observed, the sampled water was oxygen free in all sampling depths.
To test whether the right batch of pore water was sampled and as a proof that pore water sampling had no effect on pore water velocity, EC was measured manually in each of the extracted pore water samples and compared to EC data from the EC-lances. No significant variation was observed, the diurnal EC pattern was highly similar.

Validation of the UPLC-MS/MS method has taken place using:

1. Pore water and surface water samples from Erpe river (Berlin, Germany).
2. Effluent water samples from Käppala WWTP (Stockholm, Sweden).

Matrix effects on LC retention times RT were observed and quantified. The use of internal standards allows us to correct for RT shifting.
Spike/recovery experiments are currently conducted using quality control standards (QC). They are prepared by spiking Erpe water from a location upstream of the WWTP effluent outlet.

Accuracy of the method is evaluated by calculating the percent deviation from the nominal QC concentrations. Precision is determined by calculating the coefficient of variation (CV) of replicates within one sample run (intra-day) and between sample runs (inter-day).

f. Publication status

- The work will be published as (a) peer-reviewed article(s).
- Preliminary data were presented at the 2016 SETAC Europe Conference (Nantes, France, 22-26 May).

g. Literature

Li, Zhe, Anna Sobek, and Michael Radke. Flume experiments to investigate the environmental fate of pharmaceuticals and their transformation products in streams. Environmental Science & Technology 49.10 (2015): 6009-6017.

Duff, John H., et al. A mini drivepoint sampler for measuring pore water solute concentrations in the hyporheic zone of sand-bottom streams. Limnology and Oceanography 43.6 (1998): 1378-1383.

Schwientek, Marc, et al. A high-precision sampling scheme to assess persistence and transport characteristics of micropollutants in rivers. Science of the Total Environment 540 (2016): 444-454.

Table 1. *Overview over parent compounds and related transformation products/metabolites that will be analyzed.*

Parent Compounds	**Transformation Products and Metabolites**
Ibuprofen	1OH-Ibuprofen, 2OH-Ibuprofen, 3OH-Ibuprofen, Carboxy-Ibuprofen, 4´-Isobutylacetophenone, Ibuprofen Acyl-β-D-glucuronide,
Diclofenac	Diclofenac Amide, 4'-Hydroxy-Diclofenac, Diclofenac Acyl-β-D-glucuronide
Carbamazepine	10,11-Dihydro-10,11-dihydroxy Carbamazepine, Carbamazepine-10,11-epoxide
Metoprolol	α-Hydroxymetoprolol, Metoprolol acid
Propranolol	1-Naphthol
Hydrochlorothiazide	Chlorothiazide, 4-Amino-6-chloro-1,3-benzendisulfonamide
Bezafibrate	4-chlorobenzoic-acid
1H-Benzotriazol	1H-benzotriazole-1-methanol, 1H-1-2-3-Triazole-4-5-dicarboxylic acid, 4-Hydroxy-1H-benzotriazole
Valsartan	Valsartan acid
Metformin	Guanyl Urea, 1-Methylbiguanide
Sulfamethoxazol	Sulfamethoxazol-acyl-glucuronide
Furosemide	Saluamine
Acesulfame, 1-Methyl-1H-Benzotriazol, Naproxen, Ketoprofen, Gemfibrozil, Clofibric acid	

Table 2: *List of stable isotope labeled standards that are used for quantification.*

Stable Isotope Labeled Standards
1H-Benzotriazole-D4
Acesulfame-D4
Bezafibrate-D4
Carbamazepine-D8
Clarithromycin-D3
Clofibric acid-D4
Diclofenac-13C6
Furosemide-D5
Guanylurea-15N4
Hydrochlorothiazide-C13D2
Ibuprofen-D3
Ibuprofen-D3 Acyl-β-D-Gucuronide
Ketoprofen-13CD3
Metformin-D6
Metoprolol Acid-D5
Metoprolol-D7
Naproxen-D3
Propranolol-D7
Sulfamethoxazole-Acyl-Glucuronde-D3
Sulfamethoxazole-D4
Valsartan-D3

Table 3: *Summary of the analytes, the electrospray ionisation mode and selected instrument parameters* ***used***

Compound	Polarity	Precursor (m/z)	Product (m/z)
Furosemide-D5_290	Negative	334.095	289.981
Valsartan-D3_350	Negative	437.325	350.113
1H-Benzotriazole_65	Positive	120.08	65.169
1H-Benzotriazole-D4	Positive	124.25	96.1
1-Methyl-1H-Benzotriazole_77	Positive	134.09	77.113
1-naphtol125	Negative	143.125	125.018
4-chlorobenzoic acid110	Negative	155.05	110.998
4'Hydroxy-Diclofenac_265	Positive	312.055	265.802
Acesulfame_82	Negative	162.05	82.097
Acesulfame-D4 86	Negative	166.1	86.122
alpha-Hydroxy-Metoprolol_105	Positive	284.15	105.093
Bezafibrate_316	Positive	361.975	316.007
Bezafibrate_D4_114	Positive	266	114.979
Bezafibrate_D4_132	Positive	266	132.014
Bezafibrate_D4_320	Positive	366.18	320.094
Carbamazepin_D8_202	Positive	245.175	202.141
Carbamazepine_194	Positive	237.09	194.119
Chlorothiazide_215	Negative	293.95	214.951
Clarithromycin_590	Positive	748.455	590.365
Clarithromycin-D3	Positive	751.6	593.376
Diclofenac_250	Negative	293.945	249.925
Diclofenac-13C6_255	Negative	300.05	255.952
Diclofenac-Glucuronide_215	Positive	472.015	215.012
Epoxi-Carbamazepin_180	Positive	253.1	180.075
Furosemide 284	Negative	328.95	284.923
Guanyl Urea_15N5_63	Positive	107.095	63.166
Guanylurea_60	Positive	103.075	60.197
Hydrochlorothiazide_269	Negative	296	268.878
Hydrochlorothiazide_C13D2_270	Negative	300.05	270.93
Ibuprofen-D3 Glucuronide_85	Negative	384.25	85.1
Ketoprofen-13CD3_213	Positive	259.075	213.13
Metformin_71	Positive	130.11	71.165
Metformin_D6_59	Positive	136.185	59.214
Metoprolol Acid_191	Positive	268.14	191.019
Metoprolol_133	Positive	268.16	133.08
Naproxen_170	Negative	229.15	170.055
Propranolol_116	Positive	260.175	116.15
Propranolol_155	Positive	260.125	155.098
Saluamine_204	Negative	249	204.936
Sufamethoxazole_92	Positive	254.025	92.106
Sulfamethoxazole_D4_96	Positive	258.075	96.125
Sumfamethoxazole-Glucuronide_156	Positive	430.11	156.047
Valsartan acid_165	Negative	265.135	165.081
Valsartan_350	Negative	434.3	350.116

4. Sorption of Micropollutant in River Sediment

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a. Aim

The aim of this method is to evaluate sorption of selected pharmaceuticals in hyporheic river sediment. Sorption process is expected to be one of main important factors in conjunction with degradation process, in the downward movement of micropollutants in sediment that receives treated wastewater such as Heidemühle, Berlin. This method will determine equilibrium concentrations in aqueous and solid soil phases which eventually generate adsorption isotherms for each micropollutant compounds studied.

b. Sediment sampling

Sediment and water samples were taken from river located in Heidemühle, Berlin during JFE in June 2016. The upper layer of sediment (about 15 cm) were taken using soil column sampler. These samples were taken in the same location together with ESR 8 (Cyrus Njeru) where he will be studying microbial degradation of selected micropollutants.

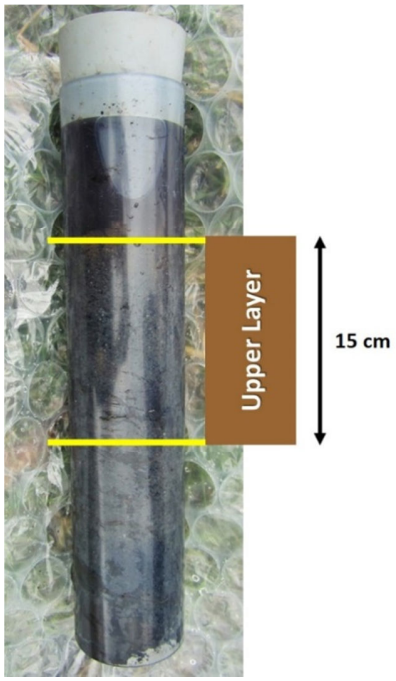

Figure 8. Soil column sampler

c. Batch adsorption experiment

Air-dried sediment samples (5 g) were mixed with 10 mL, 20 mL and 100mL Mili-Q water/river water in 100 mL glass amber bottle. 100µL of several concentration levels of diclofenac were spiked into Mili-

Q/river water for producing final concentration at 10ppb, 50ppb and 100ppb. The experiments were run in triplicates and also include control samples as for reference. The sediment and water were continuously mixed using orbital shaker for 24 and 48 hours at room temperature (Xu et al., 2009; Revitt et al., 2015).

Figure 2. Batch adsorption experiment

d. Sample extraction

The filtered aqueous samples were passed through HyperSep C18 cartridge (500 mg/6 ml, Thermo Scientific). The cartridges were previously pre-conditioned with 3 mL of ethyl acetate, 3 mL of methanol, and 3 mL of de-ionized water (pH 3) in sequence. The cartridge was dried by nitrogen for 10 min after sample loading, and followed with 8 mL of ethyl acetate elution. The elution samples were dried by using anhydrous sodium sulphate for eliminating any water presence. Next, the samples were reduced to 0.5 mL with a gentle stream of nitrogen, and then transferred into GC vial. 100 µL of MTBSTFA (N-tert-Butyldimethylsilyl-N-methyltrifluoroacetamide) was added as derivatization agent, and followed by addition of ethyl acetate until 1.0 mL. The GC vials were put into oven at 70 ◦C for 60 minutes for derivatization (Xu et al., 2009).

e. Instrumental analysis

Diclofenac was determined using an Agilent 7890A GC with 5975C MSD equipped with an HP-5MS GC column (30 meter, 0.25 mm internal diameter, 0.25 µm film thickness). Helium was used as the carrier gas with a column flow rate of 1.0 mL/min. Injector temperature was 250 ◦C, and the interface and ion source temperatures were set at 280 and 230 ◦C, respectively. The GC oven temperature programme was optimized based on Xu et al. (2009), where the initial temperature was kept at 50 ◦C for 1 min, followed by the first ramp at 20 ◦C/min to 120 ◦C, second ramp at 10 ◦C/min to 280 ◦C, and holding for 5 min. Prior to quantification process, full scan mode was employed ranging from m/z 50 to 500 for obtaining mass spectra and GC retention time of diclofenac. Then, the base peak was selected and two more ions were selected for confirmation. For quantification, the MS was operated in the selected ion monitoring (SIM) mode with electron impact ionization voltage of 70 eV. A 2 µL sample was injected in pulsed splitless mode.

f. Publication status

The work will be published as (a) peer-reviewed article(s).

g. Literature

Jian Xu, Laosheng Wu and Andrew C Chang. Degradation and adsorption of selected pharmaceuticals and personal care products (PPCPs) in agricultural soils. 2009. Chemosphere 77: 1299-1305

Michael Revitt, Tamas Balogh and Huw Jones. Sorption behaviours and transport potentials for selected pharmaceuticals and triclosan in two sterilised sediments. 2015. Journal of Soils and Sediments 15: 594-606