Supporting Information for
Analytical Chemistry

Molecularly-imprinted polymers for compound-specific isotope analysis of organic micropollutants in aquatic enviroments

Rani Bakkour[1,2], Jakov Bolotin[1], Börje Sellergren[3], and Thomas B. Hofstetter[1,2*]

[1]Eawag, Swiss Federal Institute of Aquatic Science and Technology, Dübendorf, Switzerland, [2]Institute of Biogeochemistry and Pollutant Dynamics (IBP), ETH Zürich, Zürich, Switzerland, [3]Department of Biomedical Sciences, Malmö University, Malmö, Sweden

*Corresponding author: thomas.hofstetter@eawag.ch
phone +41 58 765 50 76, fax +41 58 765 50 28

6 Pages, 3 Figures, 1 Table

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S1 Chemicals

Chemicals used including their purities and suppliers follow: 1*H*-benzotriazole (99%), 5-methyl-1*H*-benzotriazole (98%), 5,6-dimethyl-1*H*-benzotriazole monohydrate (99%), ethyl acetate ($\geq$ 99.7% Chromasolv®), 2,2'-azobisisobutyronitrile (AIBN) ($\geq$ 98.0% purum), methacrylic acid (MAA) (99%), and ethylene glycol dimethacrylate (EGDMA) (98%) were purchased from Sigma-Aldrich. Sodium hydroxide ($\geq$ 99%), hydrochloric acid (32%, for analysis), sodium sulfate anhydrous ($\geq$ 99% for analysis), acetone ($\geq$ 99.8% for analysis EMSURE®), formic acid ($98-100$% for analysis EMSURE®), dichloromethane ($\geq$ 99.8% for analysis EMSURE®), toluene ($\geq$ 99.9% for analysis EMSURE®), and $n-$hexane ($\geq$ 99.9% for analysis EMSURE®), were purchased from Merck. Benzothiazole (96%), and naphthalene ($\geq$ 99%) were purchased from Aldrich. 1-methyl-benzotriazole ($\geq$ 98%) from Alfa Aesar. Methanol ($\geq$ 99.9% Optima® LC/MS), and acetonitril ($\geq$ 99.8% for HPLC ACROS Organics™), from Fisher Sienteific. An in-house standard of 1*H*-benzotriazole ($\geq$ 99% puriss. p.a.) was purchased from Fluka.

All chemicals were used as received except for MAA, EGDMA, and AIBN. AIBN was purified by recrystallization from methanol. MAA was distilled at reduced pressure between 1 and 2 mbar and temperature between 33 and 35. EGDMA was subjected to sequential extractions with aqueous solution of sodium hydroxide 10%, water, and saturated aqueous solution of sodium chloride. The purified EGDMA was subsequently dried with anhydrous sodium sulfate, filtered, and distilled between 1 and 2 mbar at 85 to 90 °C.

Carrier and reference gases for GC/IRMS were helium (99.999%), N_2 (99.9999%), CO_2 (99.999%), and H_2 (99.999%) from Carbagas (Rümlang, Switzerland). Aqueous solutions were prepared with deionized water (18.1 MΩ·cm, Barnstead NANOpure Diamond Water Purification System).

S2 Field site and sampling

For pristine river water, we sampled river Bünz in Muri AG, Switzerland, on September 23, 2014, 100 m upstream of the municipal waste water treatment plant (WWTP). Samples were collected in a 55 L bottle that had been rinsed with methanol, deionized water, and river water prior to sampling. River water aliquot of 100 mL was separated from the 55 L sample and kept in the freezer at -20 °C for chemical analysis of micropollutants and dissolved organic carbon (DOC) The remaining water were subject to the sample preparation procedures described below.

For waste water, we sampled 25 L influent and 50 L effluent of a municipal WWTP in Aadorf, TG, Switzerland, on June 10, 2015. The Aadorf WWTP consists of a sand channel, a primary clarifier, and a biological treatment step combined with a secondary clarifier. The hydraulic retention times for the WWTP were between 7 and 11 h on the day of sampling and the flow rate amounted to 7050 m^3/d. The influent water was sampled right after the bar screen before entering the sand channels, whereas the effluent water was sampled before discharge from the WWTP into the nearby creek (Lützelmurg). Aliquots for concentration measurements of micropollutants and DOC were again treated identically to river water samples while the

remaining samples were processed as shown below.

Seventeen different brands of dishwasher detergents were purchased from 7 retailers in the catchment area of the WWTP Aadorf. A list of the purchased detergents, their measured contents of 1*H*-benzotriazole can be found in Table S1.

S3 Dishwasher detergent

Table S1 List of dishwasher detergents purchased from retailers in the catchment area of WWTP Aadorf along with their measured contents of 1*H*-benzotriazole.

Retailer	**Brand name**	**Sample type**	**Sample No.**	**1H-BT concentration** (mg 1H-BT/g detergent)
Coop	Sun	tabs	A1	0.18
	Somat	tabs	A2	0.91
	Prix Garantie	tabs	A3	n.d.
	Finish powerball	tabs	A4	n.d.
	Qualité & Prix	tabs	A5	n.d.
Migros	M-Budget	tabs	B1	0.10
	M Classic	tabs	B2	0.34
	Handy matic	tabs	B3	0.18
	Handy matic	gel	B4	0.55
	Handy matic	machine care liquid	B5	n.d.
Spar	Splendid	tabs	C1	0.14
	Splendid	machine care liquid	C2	n.d.
	Sun	gel	C3	n.d.
Denner	Denner	tabs	D	0.39
Volg	Volg	powder	E	0.14
Village store	Splendid	tabs	F	0.08
Held ecover	Held ecover	powder	G	n.d.

n.d. not detected with limit of detection of 0.003 mg 1HBT/g detergent (95% confidence interval)

S4 Synthesis of molecular imprinted polymers

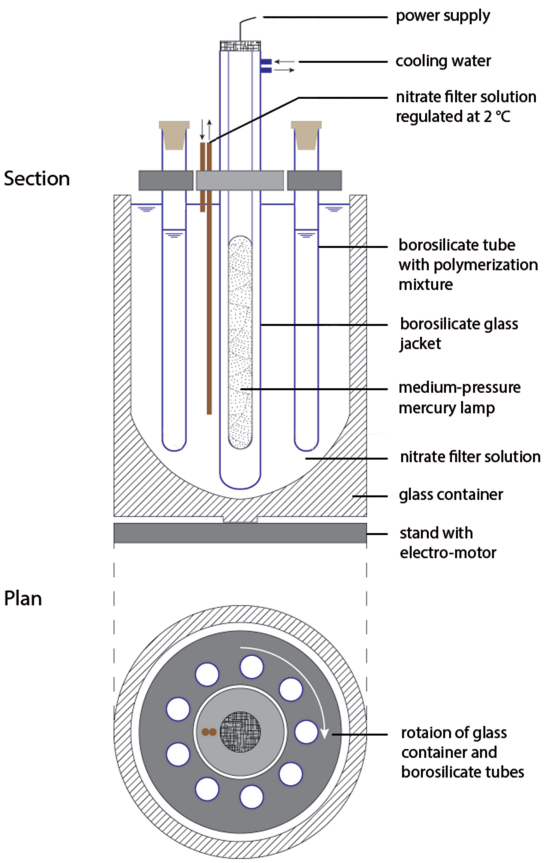

Figure S1 Merry-go-round photoreactor used for synthesis of molecularly-imprinted polymers as well as non-imprinted polymers, modified from Wegelin et al. [1]

S5 Preparation of dishwashing detergents for C and N isotope analysis of $1H$-BT

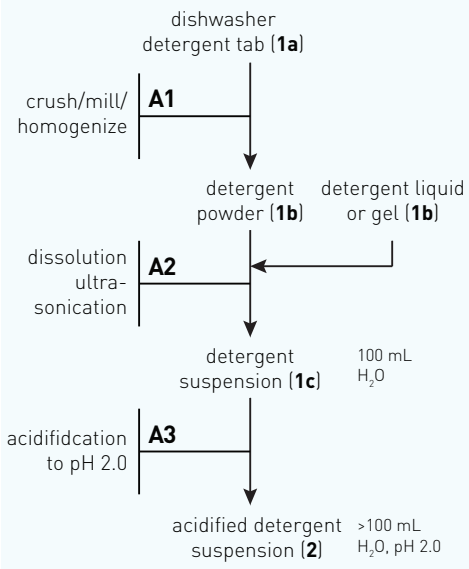

Figure S2 Specific sample preparation steps required for C and N isotope analysis of $1H$-BT in dishwashing detergents. The acidified suspensions are treated further as documented in Figure 2 of the main manuscript.

S6 Derivations of interaction enthalpies for assessment of molecularly-imprinted polymers

The enthalpies of interaction between the analytes shown in Figure S3 and the synthesized polymers, $\Delta_r H_i$, were calculated from the slope of van't Hoff equation, eq. S3, where the natural logarithm of capacity factors at variant temperatures of 278, 288, and 298 K were plotted versus the corresponding reciprocal absolute temperatures ($1/T$). Derivation of eq. S3 is shown below. The capacity factor, k_i, correlates with the equilibrium distribution coefficient, K_i, according to eq. S1[2,3]:

$$k_i = K_i \frac{V_s}{V_m} \tag{S1}$$

where V_s and V_m are volumes of the solid phase and the mobile phase, respectively. The van't Hoff equation can be written as shown in eq. S2[4]. Assuming that the ratio V_s/V_m in eq. S1 is independent of temperature, the capacity factor k_i may be written for K_i as shown in eq. S3[2,3].

$$\frac{d \ln K_i}{d\frac{1}{T}} = -\frac{\Delta_r H_i}{R} \tag{S2}$$

$$\frac{d \ln k_i}{d\frac{1}{T}} = -\frac{\Delta_r H_i}{R} \tag{S3}$$

where R is the gas constant.

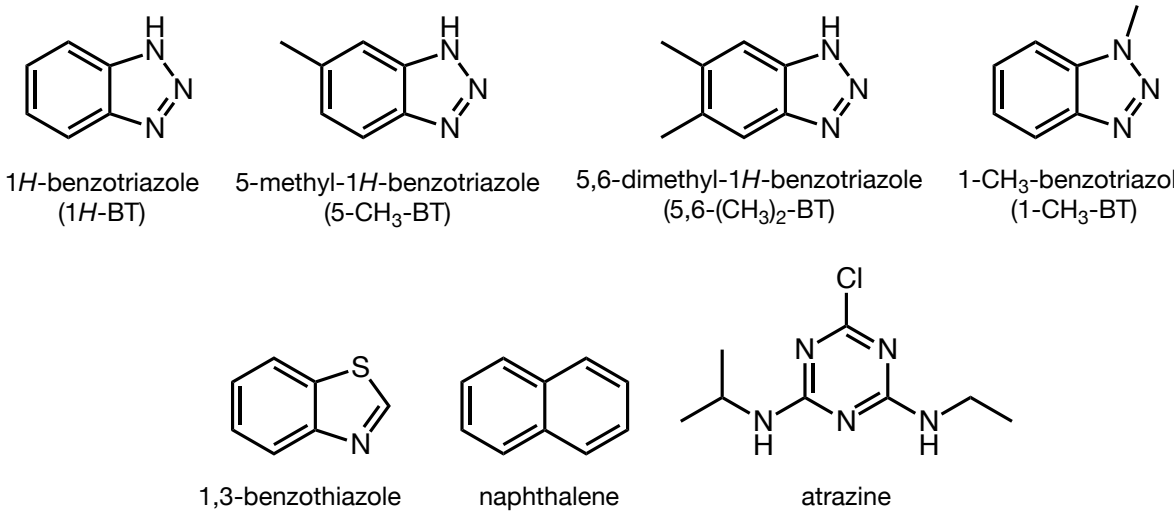

Figure S3 Molecular structures, names, and abbreviations of analytes used for the evaluation of interaction enthalpies

S7 References

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[4] Atkins, P.; de Paula, J. *Physical Chemistry*, 10th ed.; 2014.