Supplementary Material (ESI) for Journal of Environmental Monitoring


Electronic Supplementary Information

# Correlation of six anthropogenic markers in waste water, surface water, bank filtrate, and soil aquifer treatment

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**Table S1** Gradient program for the analysis of DTA.

| step | time in min | flow rate in µL/min | eluent A[a] in % | eluent B[b] in % | eluent C[c] in % |
|---|---|---|---|---|---|
| 1 | 0.0 | 200 | 80 | 10 | 10 |
| 2 | 1.0 | 200 | 80 | 10 | 10 |
| 3 | 13.0 | 200 | 0 | 90 | 10 |
| 4 | 17.0 | 200 | 0 | 90 | 10 |
| 5 | 17.1 | 200 | 80 | 10 | 10 |
| 6 | 21.0 | 200 | 80 | 10 | 10 |

[a] water with 0.1% formic acid, [b] methanol with 0.1% formic acid, [c] 50 mM ammonium acetate

**Table S2** Gradient program for the analysis of CBZ.

| step | time in min | flow rate in µL/min | eluent A[a] in % | eluent B[b] in % |
|---|---|---|---|---|
| 1 | 0.0 | 200 | 80 | 20 |
| 2 | 20.0 | 200 | 0 | 100 |
| 3 | 28.0 | 200 | 0 | 100 |
| 4 | 29.0 | 200 | 80 | 20 |

[a] water with 20 mM ammonium formiate, [b] 2/3 acetonitrile 1/3 methanol with 20 mM ammonium acetate

**Table S3** Gradient program for the analysis of BTZ and 4-Ttri.

| step | time in min | flow rate in µL/min | eluent A[a] in % | eluent B[b] in % |
|---|---|---|---|---|
| 1 | 0.0 | 100 | 70 | 30 |
| 2 | 2.0 | 100 | 70 | 30 |
| 3 | 4.0 | 100 | 20 | 80 |
| 4 | 10.0 | 100 | 20 | 80 |
| 5 | 11.0 | 100 | 70 | 30 |

[a] water with 2 mM ammonium carbonate, [b] methanol with 2 mM ammonium carbonate

**Table S4** Effluent concentrations of the secondary sedimentation basin in WWTP 5.

| **WWTP (population served)** | **throughput** | **effluent concentration secondary sedimentation basin** |
|---|---|---|
| | $m^3 d^{-1}$ | $\mu g L^{-1}$ |
| WWTP 5 (220,000) | | |
| acesulfame | 151,200 | 9.0 |
| sucralose | | 0.51 |
| carbamazepine | | 0.38 |
| diatrizoic acid | | 2.4 |
| benzotriazole | | 3.2 |
| 4-methylbenzotriazole | | 2.4 |

**Table S5** Daily loads of acesulfame in kg/d at the sampling point Basel/Switzerland based on the measured stream flow and detected concentrations at different sampling dates.

| **sampling date** | **stream flow (Q) in m³/s** | **acesulfame in µg/L** | **load in kg/d** |
|---|---|---|---|
| 12.01.2010 | 781 | 0.80 | 54 |
| 11.02.2010 | 643 | 0.91 | 51 |
| 08.03.2010 | 701 | 0.93 | 56 |
| 07.05.2010 | 1074 | 0.71 | 66 |
| 07.04.2010 | 814 | 0.74 | 52 |
| 01.06.2010 | 1688 | 0.48 | 70 |
| 01.07.2010 | 1282 | 0.64 | 71 |


**Fig. S1** Sampling points at the rivers Rhine and Main.

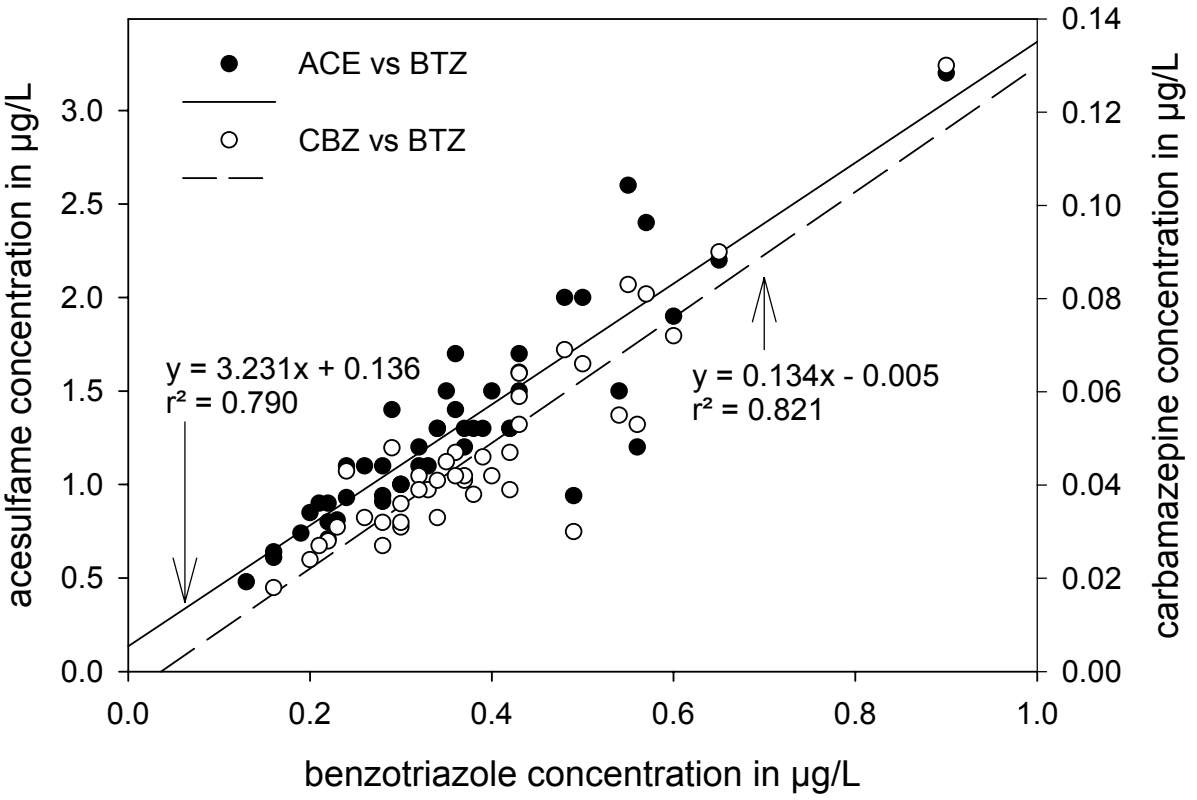


**Fig. S2** Linear regression of ACE vs BTZ and CBZ vs BTZ for all sampling points (except sampling point Basel for CBZ vs BTZ) at the rivers Rhine and Main.

| ratio ACE / CBZ | Basel | Karlsruhe | Mainz | Cologne | Düsseldorf | Lobith | Frankfurt |
|---|---|---|---|---|---|---|---|
| Basel | | X | X | X | X | X | X |
| Karlsruhe | X | | O | O | O | O | O |
| Mainz | X | O | | O | O | O | X |
| Cologne | X | O | O | | O | O | O |
| Düsseldorf | X | O | O | O | | O | O |
| Lobith | X | O | O | O | O | | X |
| Frankfurt | X | O | X | O | O | X | |

| ratio ACE / SUC | Basel | Karlsruhe | Mainz | Cologne | Düsseldorf | Lobith | Frankfurt |
|---|---|---|---|---|---|---|---|
| Basel | | O | O | X | X | X | X |
| Karlsruhe | O | | O | O | X | X | X |
| Mainz | O | O | | O | O | O | X |
| Cologne | X | O | O | | O | O | X |
| Düsseldorf | X | X | O | O | | O | X |
| Lobith | X | X | O | O | O | | O |
| Frankfurt | X | X | X | X | X | O | |

| ratio ACE / BTZ | Basel | Karlsruhe | Mainz | Cologne | Düsseldorf | Lobith | Frankfurt |
|---|---|---|---|---|---|---|---|
| Basel | | O | O | O | O | O | O |
| Karlsruhe | O | | O | O | O | O | O |
| Mainz | O | O | | O | O | O | O |
| Cologne | O | O | O | | O | O | O |
| Düsseldorf | O | O | O | O | | O | O |
| Lobith | O | O | O | O | O | | X |
| Frankfurt | O | O | O | O | O | X | |

| ratio BTZ / CBZ | Basel | Karlsruhe | Mainz | Cologne | Düsseldorf | Lobith | Frankfurt |
|---|---|---|---|---|---|---|---|
| Basel | | X | X | X | X | X | O |
| Karlsruhe | X | | O | O | O | O | O |
| Mainz | X | O | | O | O | O | O |
| Cologne | X | O | O | | O | O | O |
| Düsseldorf | X | O | O | O | | O | O |
| Lobith | X | O | O | O | O | | O |
| Frankfurt | O | O | O | O | O | O | |

**Fig. S3** Statistical analysis of the calculated ratios by one-factor variance analyses and Tukey-Test with $p<0.05$. X = significantly different, O = not significantly different.

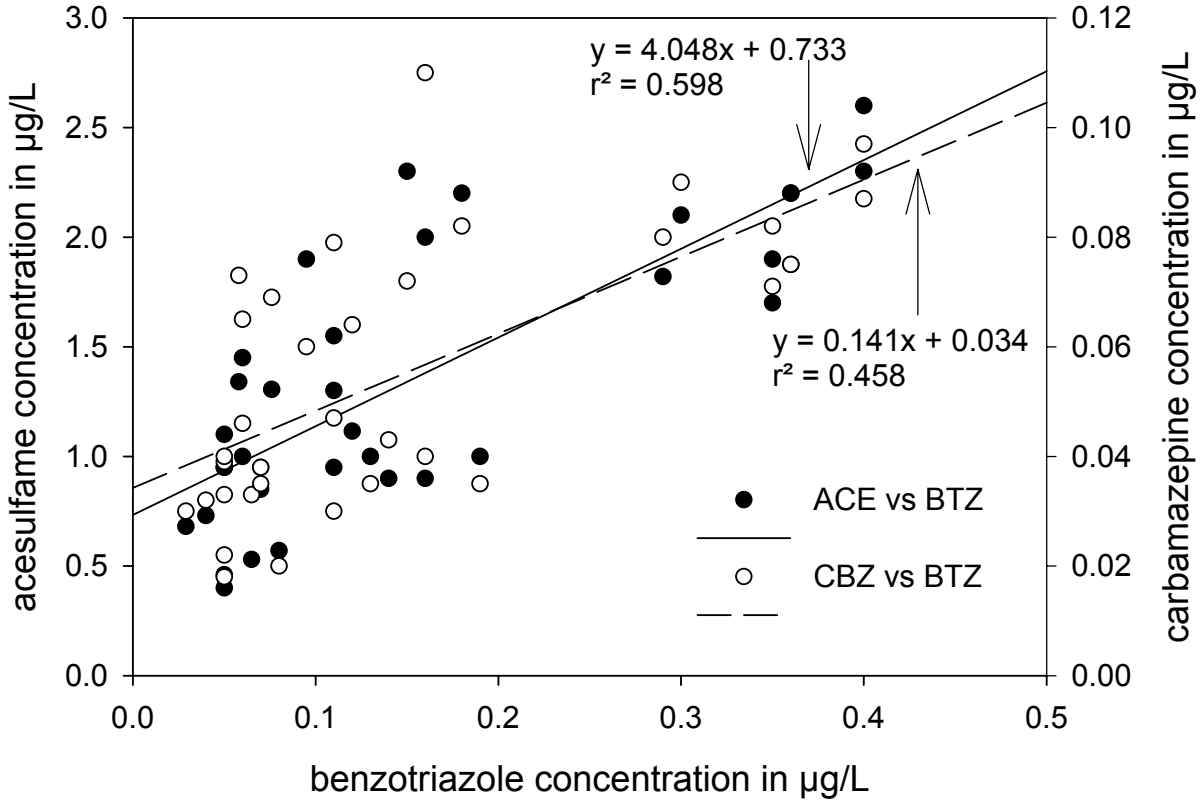


**Fig. S4** Linear regression of ACE vs BTZ and CBZ vs BTZ for RBF sampling points along the Rhine river and wells in Bavaria taken from Bayerisches Landesamt für Umwelt.[29]

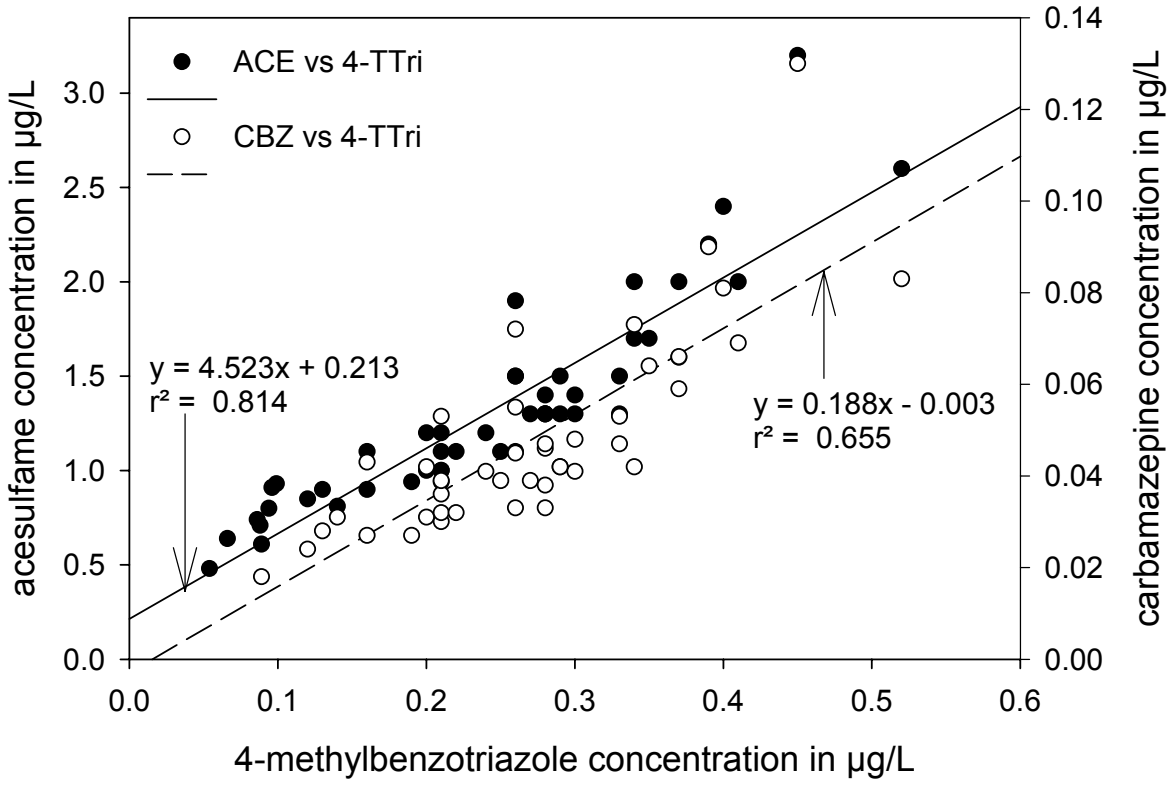


**Fig. S5** Linear regression of ACE vs 4-TTri and CBZ vs 4-TTri for all sampling points (except sampling point Basel for CBZ vs 4-TTri) at the rivers Rhine and Main.

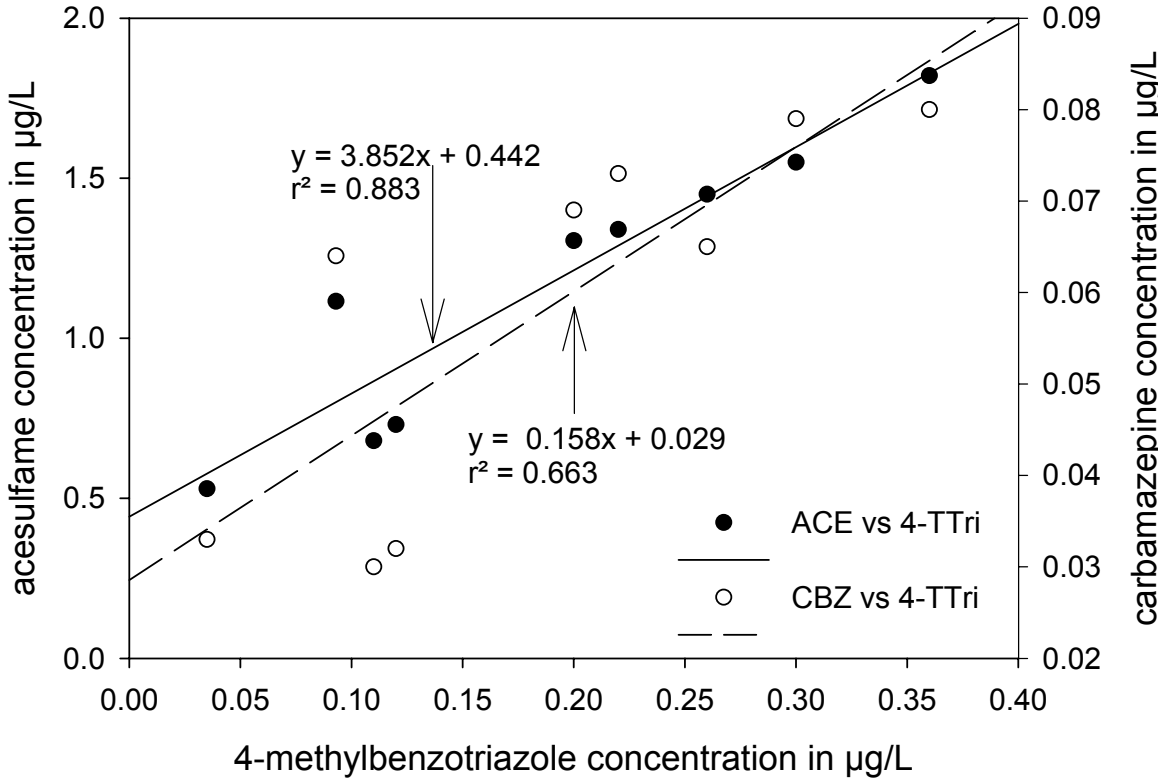


**Fig. S6** Linear regression of ACE vs 4-TTri and CBZ vs 4-TTri for all RBF sampling points at the Rhine river.