



*Supplement of*

## **Improving soil aquifer treatment efficiency using air injection into the subsurface**

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## S1 Conversion from actual to standard volumetric flow rate

$$(S1) Q_{std} = Q_{actual} \frac{P_{actual} T_{std}}{P_{std} T_{actual}}$$

Where  $Q_{std}$  is the standard volumetric flow rate in standard liters per minute (SLPM),  $Q_{actual}$  is the measured volumetric flow rate in liters per minute (LPM),  $P_{actual}$  is the measured pressure (bar), and  $T_{actual}$  is the measured temperature (K).  $P_{std}$  and  $T_{std}$  were taken as 1 bar and 273.15 K - the standard pressure and temperature defined by the international union of pure and applied chemistry (IUPAC; (Ewing et al., 1994).

## S2 Contaminants of emerging concern (CECs) analysis

LC separation of Ibuprofen (IBP) was conducted by using a mixture of methanol (MeOH) and 1% (V/V) formic acid (FA) solution as a mobile phase. The gradient program was as follows: constant 50% MeOH and 50% FA solution during 0.5 min, then changes of 50–100% MeOH, 50–0% FA solution were taken in 0.5-8 min. 100% content of MeOH was kept until 10 min and then restored to 50% at 11 min. Constant 50% MeOH and 50% FA solution was kept for 4 min (11-15 min.). Electrospray mass data were acquired in the negative mode with a spray voltage of -4.2 kV. The source temperature was 500°C. N<sub>2</sub> was used as the curtain gas (setting 35), IonSource gas 1 (GS1 gas setting 60) and IonSource gas 2 (GS2 gas setting 40). MS/MS was performed using N<sub>2</sub> as collision gas (CAD gas setting 3). Other specific operating conditions are shown in Table S1.

**Table S1.** Optimized LC-MS/MS parameters for IBP

	IBP <sup>a</sup>	IBP <sup>b</sup>
[M-1]/Fragment Ion (m/z)	205.1/159.1	205.1/161.1
Delustering potential DP (V)	-18	-18
Entrance potential EP (V)	-10	-10
Collision energy (rel. units)	-15	-15
Collision cell exit potential CXP (V)	-4	-4
Retention time (RT)	10.96	10.96

<sup>a</sup> for quantitation. <sup>b</sup> for qualitative identification.

LC separation of Carbamazepine (CBZ) and Benzotriazole (BTR) was also conducted by using a mixture of methanol (MeOH) and 1% (V/V) formic acid (FA) solution as a mobile phase. The gradient program was as follows: constant 5% MeOH and 95% FA solution for 2 min, then changes of 5–100% MeOH, 95–0% FA solution were taken in 2–7 min. 100% content of MeOH was kept until 11 min and then restored to 5% at 13 min. Constant 5% MeOH and 95% FA solution was kept for 6 min

25 (13-19 min). Electrospray mass data were acquired in the positive mode with a spray voltage of 5.5 kV. The source temperature was 550°C. N<sub>2</sub> was used as the curtain gas (setting 30), IonSource gas 1 (GS1 gas setting 50) and IonSource gas 2 (GS2 gas setting 60). MS/MS was performed using N<sub>2</sub> as collision gas (CAD gas setting 10). Other specific operating conditions are shown in Table S2.

**Table S2.** Optimized LC-MS/MS parameters for CBZ and BTR

	CBZ <sup>a</sup>	CBZ <sup>a</sup>	BTR <sup>a</sup>	BTR <sup>b</sup>
[M+1]/Fragment Ion (m/z)	237.1/194.1	237.1/193.1	120.1/65.2	120.1/92.0
Delustering potential DP (V)	40	40	42	42
Entrance potential EP (V)	10.5	10.5	10.5	10.5
Collision energy (rel. units)	25	25	32	23
Collision cell exit potential CXP (V)	4	4	2.5	5.0
Retention time (RT)	10.5	10.5	9.24	9.24

<sup>a</sup> for quantitation. <sup>b</sup> for qualitative identification.

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### S3 Synthetic effluent composition

**Table S3.** Basic parameters of the synthetic effluent – mean  $\pm$  SD

Experiment	[NH <sub>4</sub> <sup>+</sup> ] (mg-N L <sup>-1</sup> )	[TKN] (mg L <sup>-1</sup> )	[NO <sub>3</sub> <sup>-</sup> ] (mg-N L <sup>-1</sup> )	[TN] (mg L <sup>-1</sup> )	[DOC] (mg L <sup>-1</sup> )
FDO	2.46 $\pm$ 0.95	8.94 $\pm$ 0.66	1.53 $\pm$ 0.37	10.48 $\pm$ 0.88	41.61 $\pm$ 1.38
AI-LF <sub>1</sub>	1.83 $\pm$ 0.43	9.03 $\pm$ 0.21	0.12 $\pm$ 0.01	9.16 $\pm$ 0.21	41.50 $\pm$ 0.99
AI-HF <sub>1</sub>	3.61 $\pm$ 0.49	8.20 $\pm$ 0.07	0.66 $\pm$ 0.09	8.88 $\pm$ 0.11	40.37 $\pm$ 1.49
AI-HF <sub>2</sub>	4.19 $\pm$ 0.29	8.42 $\pm$ 0.30	0.96 $\pm$ 0.41	9.39 $\pm$ 0.17	39.82 $\pm$ 0.69
AI-HF <sub>3</sub>	2.96 $\pm$ 0.44	7.66 $\pm$ 0.79	0.71 $\pm$ 0.04	8.37 $\pm$ 0.78	40.66 $\pm$ 3.35
AI-LF <sub>2</sub>	3.68 $\pm$ 0.51	8.30 $\pm$ 0.20	0.81 $\pm$ 0.14	9.12 $\pm$ 0.10	42.56 $\pm$ 1.59

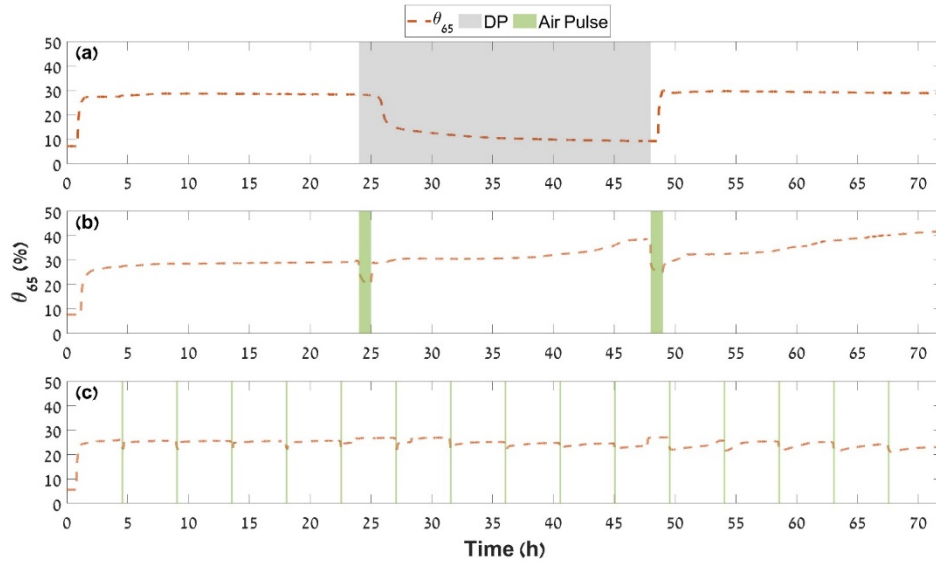
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**Table S4.** Concentrations of emerging contaminants in the synthetic effluent – mean  $\pm$  SD

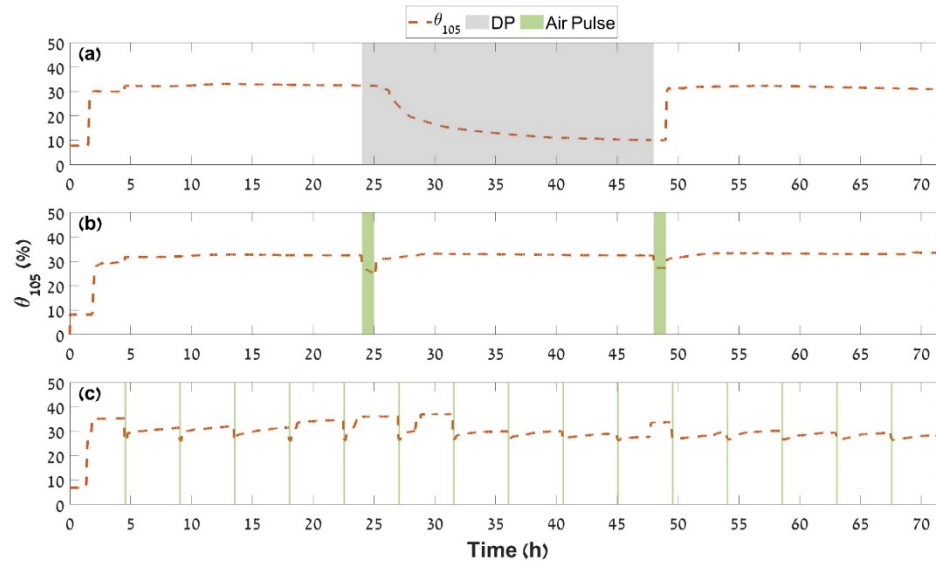
Experiment	[IBP] ( $\mu$ g L <sup>-1</sup> )	[CBZ] ( $\mu$ g L <sup>-1</sup> )	[BTR] ( $\mu$ g L <sup>-1</sup> )
FDO <sup>a</sup>	0.76 $\pm$ 0.03	1.66 $\pm$ 0.04	7.37 $\pm$ 2.24
AI-LF <sub>1</sub>	1.45 $\pm$ 0.08	1.05 $\pm$ 0.05	9.48 $\pm$ 0.47
AI-HF <sub>1</sub>	1.06 $\pm$ 0.14	0.91 $\pm$ 0.07	9.05 $\pm$ 0.43
AI-HF <sub>2</sub>	0.80 $\pm$ 0.09	1.08 $\pm$ 0.04	8.90 $\pm$ 0.44
AI-HF <sub>3</sub>	71.57 $\pm$ 6.97	1.24 $\pm$ 0.02	8.43 $\pm$ 0.25
AI-LF <sub>2</sub>	65.00 $\pm$ 3.78	2.25 $\pm$ 0.08	4.83 $\pm$ 0.30

<sup>a</sup> In FDO, samples were taken and analyzed for only one replicate

55 S4 Volumetric water content (VWC) at various depths during the three main experiments

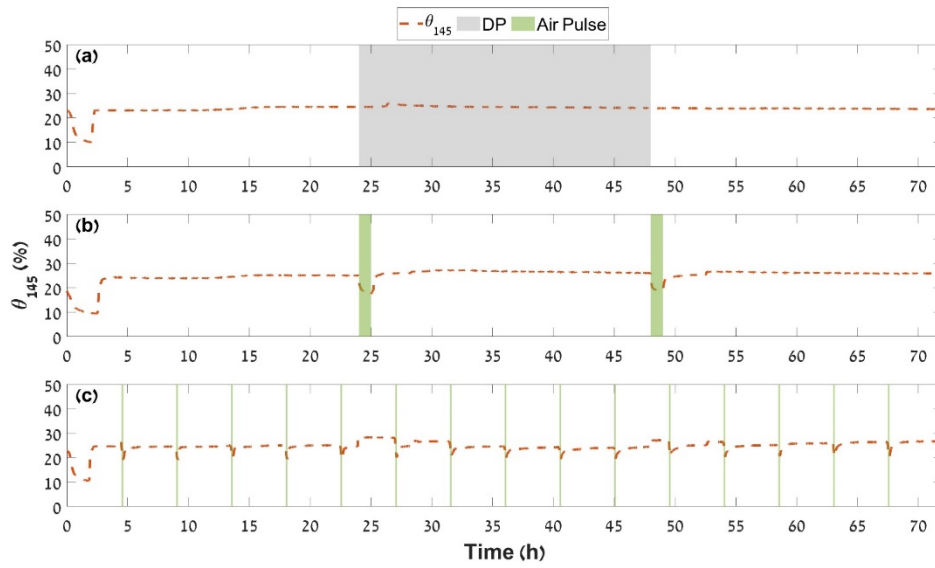


**Fig. S1.** VWC at a depth of 65 cm below soil surface ( $\theta_{65}$ ) during FDO, AI-LF<sub>1</sub> and AI-HF<sub>1</sub> (panels **a**, **b** and **c**, respectively). Gray areas symbolize DP, while green areas symbolize the air pulses.



**Fig. S2.** VWC at a depth of 105 cm below soil surface ( $\theta_{105}$ ) during FDO, AI-LF<sub>1</sub> and AI-HF<sub>1</sub> (panels **a**, **b** and **c**, respectively). Gray areas symbolize DP, while green areas symbolize the air pulses.

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**Fig. S3.** VWC at a depth of 145 cm below soil surface ( $\theta_{145}$ ) during FDO, AI-LF<sub>1</sub> and AI-HF<sub>1</sub> (panels **a**, **b** and **c**, respectively). Gray areas symbolize DP, while green areas symbolize the air pulses.

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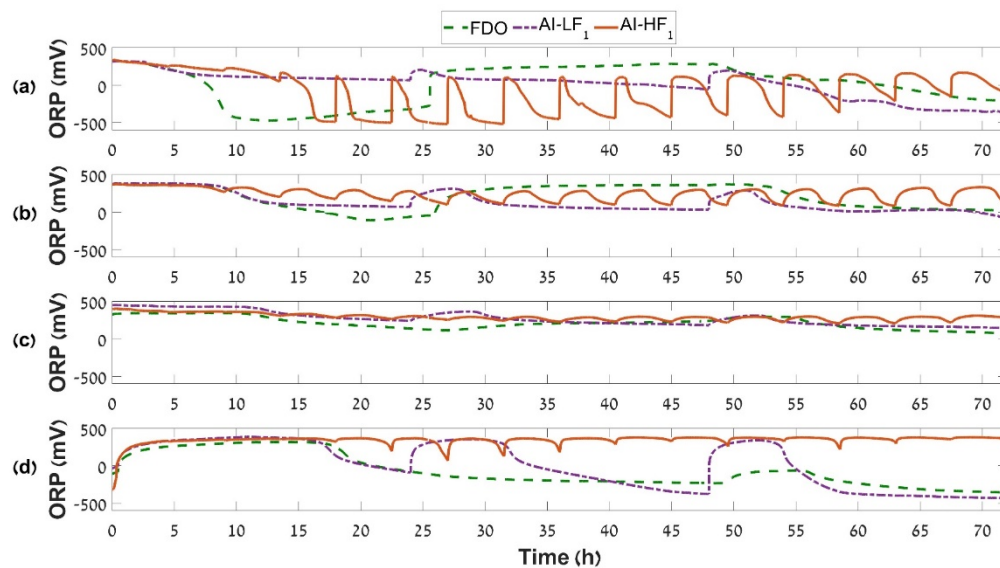
### S5 Infiltrated volumes and mean infiltration rates

**Table S5.** Infiltrated volumes and mean infiltration rates throughout each experiment

Time (h)	0-24	24-48	48-72
Experiment	Infiltrated volume in L (mean infiltration rate in cm h <sup>-1</sup> )		
FDO (1)	95 (20.30)	0 (0)	91 (19.44)
FDO (2)	151 (32.26)	0 (0)	81 (17.31)
AI-LF <sub>1</sub>	96 (20.51)	132 (28.20)	129 (27.56)
AI-HF <sub>1</sub>	111 (23.71)	97 (20.72)	67 (14.31)
AI-HF <sub>2</sub>	92 (19.66)	89 (19.01)	69 (14.53)
AI-HF <sub>3</sub>	103 (22.01)	71.5 (15.28)	54 (11.54)
AI-LF <sub>2</sub>	120 (25.64)	112.5 (24.03)	103 (22.01)

## S6 Oxidation-reduction potential (ORP) at various depths during the three main experiments

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**Fig. S4.** ORP vs. Ag/AgCl at depths of 25, 65, 105 and 145 cm below soil surface (panels **a**, **b**, **c**, and **d**, respectively) during FDO, AI-LF<sub>1</sub> and AI-HF<sub>1</sub>.

## S7 Surface head (SH) during the three main experiments

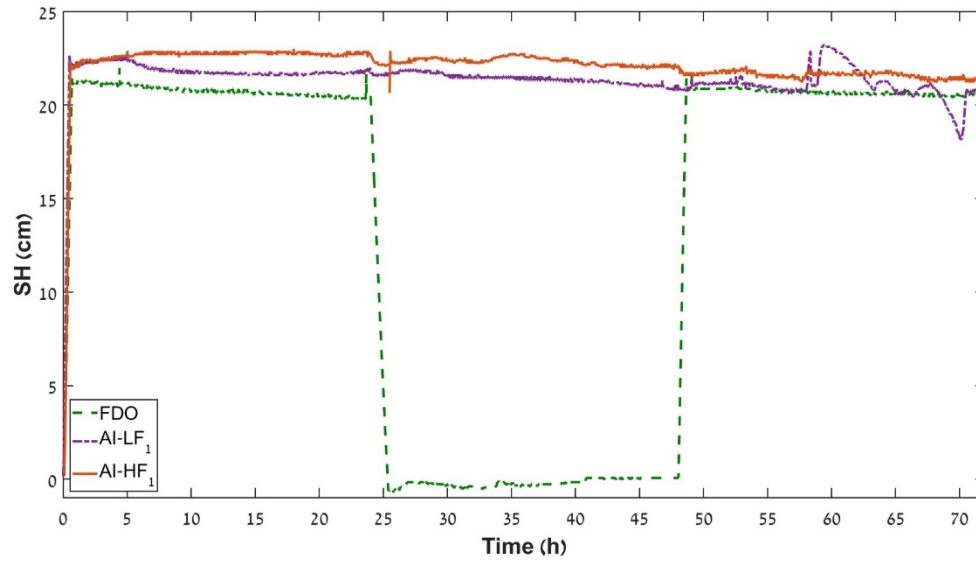
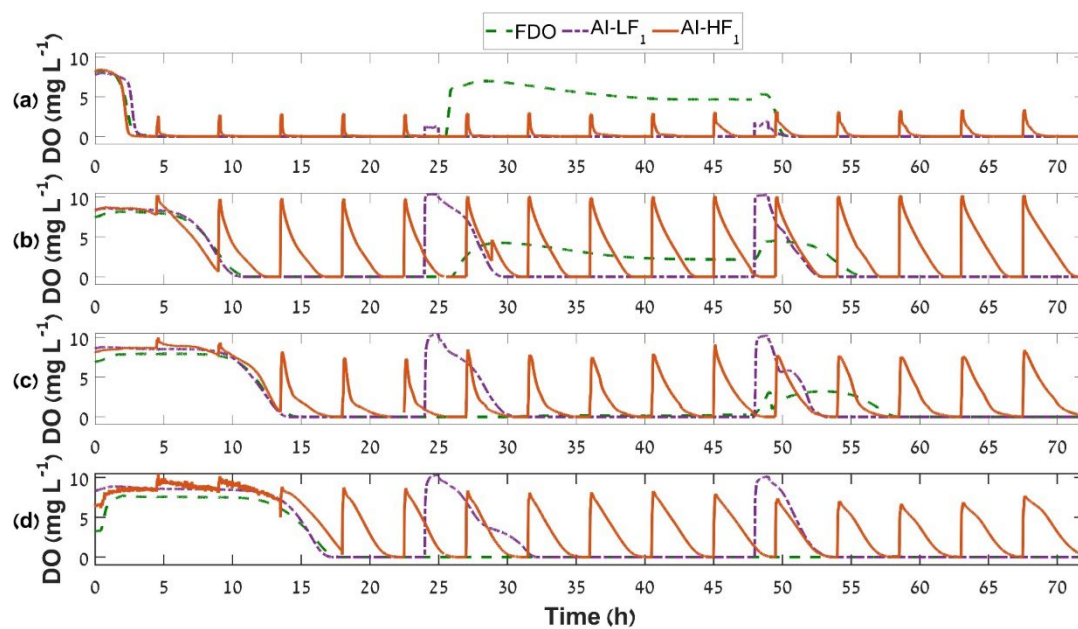


Fig. S5. Surface head (SH) during FDO, AI-LF<sub>1</sub> and AI-HF<sub>1</sub>.

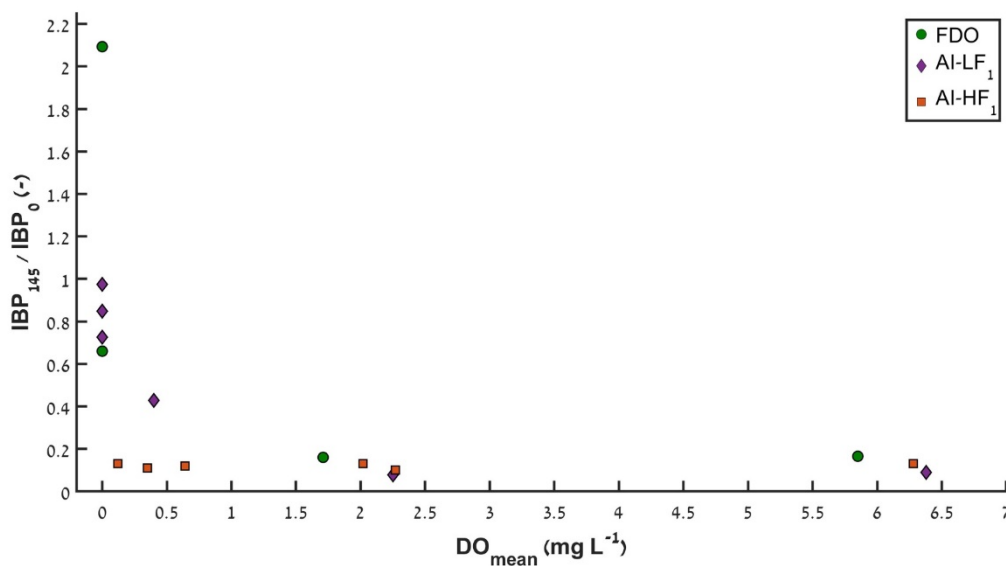


## S8 Dissolved oxygen (DO) during the three main experiments



**Fig. S6.** DO at depths of 25, 65, 105 and 145 cm below soil surface (panels **a**, **b**, **c**, and **d**, respectively) during FDO, AI-LF<sub>1</sub> and AI-HF<sub>1</sub>.

## S9 Effluent quality



**Fig. S7.** IBP concentration at a depth of 145 cm vs. the mean DO throughout the column, during FDO, AI-LF<sub>1</sub> and AI-HF<sub>1</sub>. The concentration is normalized to the inlet concentration. Values below detection limit (DL) were regarded with DL/2. In FDO, samples were taken and analyzed for only one replicate

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**Table S6.** Basic parameters of the effluent at a depth of 145 cm, normalized to the inlet concentration – mean ± SD

Experiment	[TKN] (-)	[NO <sub>3</sub> <sup>-</sup> ] (-)	[TN] (-)	[DOC] (-)
FDO	0.51 ± 0.38	0.45 ± 0.74	0.50 ± 0.25	0.14 ± 0.08
AI-LF <sub>1</sub>	0.62 ± 0.30	2.13 ± 3.46	0.64 ± 0.28	0.23 ± 0.18
AI-HF <sub>1</sub>	0.11 ± 0.13	5.63 ± 1.67	0.58 ± 0.13	0.05 ± 0.01
AI-HF <sub>2</sub>	0.15 ± 0.10	3.30 ± 1.92	0.47 ± 0.20	0.05 ± 0.05 <sup>90</sup>
AI-HF <sub>3</sub>	0.65 ± 0.29	0.57 ± 1.29	0.64 ± 0.18	0.16 ± 0.06
AI-LF <sub>2</sub>	0.72 ± 0.34	0.26 ± 0.62	0.68 ± 0.25	0.37 ± 0.22

<sup>a</sup> Values below the quantitation limit (QL) were regarded with QL/2.

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**Table S7.** Concentrations of CECs in the effluent at a depth of 145 cm, normalized to the inlet concentration – mean<sup>a</sup> ± SD

Experiment	[IBP] (-)	[CBZ] <sup>b</sup> (-)	[BTR] <sup>b</sup> (-)
FDO <sup>c</sup>	0.77 ± 0.91	0.91 ± 0.02	0.79 ± 0.33
AI-LF <sub>1</sub>	0.52 ± 0.39	0.99 ± 0.14	0.99 ± 0.07
AI-HF <sub>1</sub>	0.12 ± 0.01	0.92 ± 0.13	0.81 ± 0.05
AI-HF <sub>2</sub>	0.16 ± 0.02	1.00 ± 0.11	0.91 ± 0.09
AI-HF <sub>3</sub> <sup>d</sup>	0.89 ± 0.02	-	-
AI-LF <sub>2</sub>	0.84 ± 0.27	0.97 ± 0.03	0.94 ± 0.01

<sup>a</sup> Values below the detection limit (DL) were regarded with DL/2.

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<sup>b</sup> The first sample from each experiment (taken at  $t \sim 4.3$  h) was excluded as an outlier since it showed much lower concentrations than the others, apparently due to retardation of CBZ and BTR as a result of their interactions with soil components.

<sup>c</sup> In FDO, samples were taken and analyzed for only one replicate.

<sup>d</sup> For AI-HF<sub>3</sub>, CBZ and BTR samples were analyzed only at the inflow.

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## References

Ewing, M. B., Lilley, T. H., Olofsson, G. M., Ratzsch, M. T., and Somsen, G.: Standard quantities in chemical thermodynamics. Fugacities, activities and equilibrium constants for pure and mixed phases (IUPAC Recommendations 1994), *Pure Appl. Chem.*, 66, 533–552, <https://doi.org/10.1351/pac199466030533>, 1994.

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