

# **Supporting Information: Multiple barriers for micropollutants in nutrient recovery from centrate - combining membrane bioreactor and electro dialysis**

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## **Key words:**

reject water, nitrogen recovery, trace pollutants, heavy metals, wastewater, nutrient  
center

## **Chemicals and Analytical Standards**

Ultrapure water, generated using a Merck MilliQ Integral 5 System (Merck, Darmstadt, Germany), served as the base for diluting all samples, including those for salts, nutrients, and metals analysis. Furthermore, it was used as the eluent A in the LC-MS/MS gradient. UPLC-grade methanol (BioSolve, Valkenswaard, Netherlands) was employed as eluent B in the mobile phase.

For LC-MS/MS analysis of micropollutants, analytical standard stock solutions were prepared either in methanol or a water/methanol mixture, and then stored at -20 °C until calibration standards were created. In the case of ICP-MS analysis, a blend of analytical standards (Spex 1, Spex 2a, Spex 3, Spex 4; SpexCertiprep, Metuchen, USA) & Merck VI (Merck, Darmstadt, Germany) was formulated for calibration in an aqueous solution containing 1% HNO<sub>3</sub> (HNO<sub>3</sub> (60%), Ultrapur, Merck, Darmstadt, Germany). Individual-element analytical standards for elemental analysis via ICP-OES were procured from Merck (Darmstadt, Germany) as well.

## Tables

Tab. SI 1: Recovery of analytes for Sartorius RC25 filters used in this study. Each matrix was spiked with 10  $\mu\text{L}$  of 1  $\text{ng}/\mu\text{L}$  mixed reference standard and filtered through the RC25

	Recovery in centrate	Recovery in tap water
4-Acetoaminoantipyrine	97.5( $\pm$ 1.8)%	105.7( $\pm$ 7.6)%
4/5-Methylbenzotriazole	92.6( $\pm$ 2.57)%	116.7( $\pm$ 9.32)%
Acesulfame	100.4( $\pm$ 2.31)%	104.9( $\pm$ 6.75)%
Acetaminophen	100.6( $\pm$ 3.51)%	102.1( $\pm$ 8.23)%
Benzotriazole	96.9( $\pm$ 4.44)%	n.d.%
Carbamazepine	95.4( $\pm$ 2.98)%	106( $\pm$ 9.07)%
Candesartan	n.d.	n.d.
Diclofenac	40.3( $\pm$ 2.12)%	107.3( $\pm$ 11.3)%
Ep-Carbamazepine	111.6( $\pm$ 3.88)%	106.4( $\pm$ 8.8)%
Gabapentin	101.6( $\pm$ 3.26)%	n.d.%
Gabapentin-Lactam	97.9( $\pm$ 1.83)%	106.2( $\pm$ 8.42)%
Ibuprofen	74.2( $\pm$ 2.87)%	106.2( $\pm$ 8.73)%
Lamotrigine	95.6( $\pm$ 1.74)%	101.3( $\pm$ 9.15)%

Lidocaine	96.4(±3.41)%	95(±10.08)%
Metformin	97.6(±1.41)%	104.5(±6.77)%
Metoprolol	96(±1.77)%	105.6(±8.54)%
Metoprolol Acid	99.3(±2.78)%	106.9(±9.63)%
Oxipurinol	94.2(±3.87)%	105.4(±8.17)%
tDiOH-Carbamazepine	93.8(±3.35)%	n.d.%
Tramadol	98.2(±2.48)%	106.2(±8.35)%
Valsartan	78.7(±2.33)%	n.d.%
Valsartan Acid	92.7(±1.69)%	103.3(±11.38)%

*Tab. SI 2 Recovery of inorganic compounds for Sartorius RC25 filters used in this study. Each matrix was spiked with 10  $\mu$ L of 1 ng/ $\mu$ L mixed reference standard and filtered through the RC25 filter. The filtered spiked matrix was compared against a reference that was spiked and centrifuged (15.000 rpm) for 15min. Recovery experiments were performed in triplicate.*

	<b>Recovery in %</b>
	<b>ultrapure water</b>
<b>Al</b>	131.2
<b>Cr</b>	97( $\pm$ 5.25)
<b>Co</b>	96.4( $\pm$ 6.3)
<b>Ni</b>	94.4( $\pm$ 4.81)
<b>Cu</b>	98.4( $\pm$ 0)
<b>Zn</b>	100.9( $\pm$ 4.02)
<b>As</b>	97( $\pm$ 5.25)
<b>Cd</b>	89.4( $\pm$ 1.89)
<b>Pb</b>	90.9( $\pm$ 0)

*Tab. SI 3: Gradient of liquid chromatographic separation method*

	<b>Portion in %</b>		
<b>Time in min</b>	<b>A (H2O)</b>	<b>B (MeOH)</b>	<b>Flow Rate in mL/min</b>
0.0	90	10	0.3
0.8	90	10	0.3
7.5	45	55	0.3
21.0	5	95	0.3
28.0	5	95	0.3
29.1	90	10	0.3
31.0	90	10	0.3

Tab. SI 4: MS-Parameters for all analytes, including isotopically-labelled internal standards.

	ESI- Mod e	Q1 in u	Q2 in u	RT in min	DP in V	EP in V	CE in eV	CXP in V
<b>Benzotriazole</b>	+	120,01	65,00	7,54	126	10	29	10
		120,01	91,90	7,54	126	10	23	12
<b>Benzotriazole-d4</b>	+	124,01	68,00	7,45	51	10	29	10
		124,01	69,10	7,45	51	10	33	12
<b>Metformin</b>	+	130,06	59,90	0,92	66	10	17	6
		130,06	70,90	0,92	66	10	29	14
<b>4/5- Methylbenzotriazole</b>	+	134,10	77,00	8,90	71	10	31	6
		134,10	78,90	8,90	71	10	29	10
<b>5- Methylbenzotriazole- d6</b>	+	140,06	80,90	8,90	141	10	35	12
		140,10	84,90	8,90	71	10	29	10
<b>Acetaminophen</b>	+	151,99	110,10	5,50	106	10	21	10
		151,99	65,10	5,50	106	10	41	8

<b>Gabapentin-Lactam</b>	+	153,98	95,10	9,80	131	10	31	10
		153,98	93,10	9,80	131	10	35	8
<b>Gabapentin-Lactam-d6</b>	+	160,08	101,10	9,80	126	10	31	12
		160,08	100,00	9,80	126	10	29	12
<b>Gabapentin</b>	+	172,01	154,10	4,92	36	10	19	10
		172,01	137,00	4,92	36	10	21	6
<b>Gabapentin-d4</b>	+	176,06	158,10	4,85	71	10	19	18
		176,06	139,00	4,85	71	10	23	14
<b>Lidocaine</b>	+	235,10	86,10	5,36	76	10	25	8
		235,10	57,90	5,36	76	10	47	8
<b>Carbamazepine</b>	+	237,04	194,10	10,90	106	10	25	6
		237,04	193,10	10,90	106	10	47	8
<b>Lidocaine-d10</b>	+	245,12	96,10	5,29	76	10	25	12
		245,12	64,10	5,29	76	10	57	6
<b>4-Acetoaminoantipyrine</b>	+	246,07	228,10	6,79	76	10	19	30
		246,07	83,10	6,79	76	10	45	10
<b>Carbamazepine-d10</b>	+	247,02	204,10	10,77	29	10	29	10



		247,02	202,00	10,77	56	10	47	10
<b>Ep-Carbamazepine</b>	+	253,00	180,10	9,42	71	10	43	16
		253,00	210,10	9,42	71	10	21	14
<b>Lamotrigine</b>	+	255,99	211,00	6,38	91	10	39	4
		255,99	109,00	6,38	91	10	63	6
<b>Tramadol</b>	+	264,91	58,10	6,14	86	10	49	12
		264,91	59,20	6,14	86	10	41	6
<b>Valsartan Acid</b>	+	267,00	151,00	11,08	71	10	55	18
		267,00	206,00	11,08	71	10	25	20
<b>Metoprolol Acid</b>	+	268,07	145,10	5,27	106	10	35	12
		268,07	226,10	5,27	106	10	23	28
<b>Metoprolol</b>	+	268,12	116,10	6,29	81	10	25	6
		268,12	191,10	6,29	81	10	25	4
<b>tDiOH Carbamazepine</b>	+	271,03	253,00	8,96	26	10	11	16
		271,04	180,10	8,96	86	10	43	16
<b>Metoprolol Acid-d5</b>	+	273,10	196,00	5,21	26	10	27	10
		273,10	150,10	5,21	26	10	35	16
<b>Acesulfame</b>	-	161,90	81,90	4,92	-50	-10	-20	-13

		161,90	77,90	4,92	-50	-10	-40	-13
<b>Acesulfame-d4</b>	-	165,87	86,10	4,87	-25	-10	-20	-7
		165,87	78,00	4,87	-25	-10	-46	-3
<b>Ibuprofen</b>	-	205,08	161,10	17,78	-80	-10	-10	-13
		205,08	159,10	17,78	-80	-10	-10	-13
<b>Ibuprofen-d3</b>	-	208,04	164,10	17,73	-50	-10	-10	-11
		208,04	161,10	17,73	-50	-10	-10	-15
<b>Diclofenac</b>	-	294,00	250,00	17,41	-40	-10	-16	-13
		295,88	252,00	17,41	-40	-10	-16	-11
<b>Diclofenac-d4</b>	-	297,88	254,10	17,34	-50	-10	-18	-13
		298,85	255,00	17,34	-45	-10	-20	-13
<b>Valsartan</b>	-	434,17	350,00	16,72	-40	-10	-26	-29
		434,17	178,80	16,72	-40	-10	-34	-23

*Tab. SI 5 Overview of isotope labelled standards spiked into the samples for the use as internal standard. 10 µL were spiked into every 1 mL of sample volume. The target concentration for all internal standards was 10 µg/L.*

<b>Isotopically labelled Standard</b>	<b>Used for matrix correction of ...</b>
Benzotriazole-d4	Benzotriazole
Metformin-d6	Metformin
5-Methylbenzotriazole-d6	4/5-Methylbenzotriazole
Lidocaine-d10	Lidocaine
Carbamazepine-d10	Carbamazepine
Lamotrigine-13C-15N	Lamotrigine
Valsartan Acid-d4	Valsartan Acid
Metoprolol Acid-d5	Candesartan
Acesulfame-d4	Acesulfame
Ibuprofen-d3	Ibuprofen
Diclofenac-d4	Diclofenac

Tab. SI 6: Overview of relevant physical chemical properties for analyzed micropollutants. Prediction of compounds properties computed by ChemAxon.

	<b>CAS</b>	<b>Mass</b>	<b>pK<sub>a1</sub></b>	<b>pK<sub>b1</sub></b>	<b>Isoelectric Point</b>	<b>logD (pH 5.5)</b>	<b>logD (pH 8.0)</b>
4-Acetoaminoantipyrine	83-15-8	245,282	12,5	-0,8	5,9	0,2	0,2
4/5-Methylbenzotriazole	29878-31-7	133,154	9,3	0,5	4,9	1,8	1,8
Acesulfame	33665-90-6	163,15	3,0	-6,0	0,0	-1,5	-1,5
Acetaminophen	103-90-2	151,165	9,5	-4,4	0,0	0,9	0,9
Benzotriazole	95-14-7	119,127	8,6	0,6	4,6	1,3	1,2
Carbamazepine	298-46-4	236,274	16,0	-3,8	0,0	2,8	2,8
Candesartan	139481-59-7	440,5	3,5	1,5	2,5	3,1	0,3
Diclofenac	15307-86-5	296,15	4,0	-2,1	0,0	2,7	0,9
Ep-Carbamazepine	36507-30-9	252,273	5,1	3,7	9,4	2,2	0,0

Gabapentin	60142-96-3	171,24	4,6	9,9	7,4	-1,3	-1,3
Gabapentin-Lactam	64744-50-9	153,225	14,9	-1,2	6,9	1,0	1,0
Ibuprofen	15687-27-1	206,285	4,9	0	0,0	3,1	0,8
Lamotrigine	84057-84-1	256,09	15,0	5,9	10,9	1,4	1,9
Lidocaine	137-58-6	234,343	13,8	7,8	10,8	0,6	2,6
Metformin	657-24-9	129,167	19,2	12,3	0,0	-5,7	-5,4
Metoprolol	51384-51-1	267,369	14,1	9,7	11,9	-1,4	0,1
Metoprolol Acid	56392-14-4	267,325	3,5	9,7	6,8	-1,2	-1,2
Oxipurinol	2465-59-0	152,11	6,25	2,1	7,65	-1,7	-3,2
tDiOH-Carbamazepine	176486-10-5	270,288	12,8	-3,6	0,0	0,8	0,8
Tramadol	123154-38-1	263,381	13,8	9,2	11,5	-0,9	1,2
Valsartan	137862-53-4	435,528	4,4	-0,6	1,9	4,0	0,5
Valsartan Acid	-	266,26	4,0	-1,4	1,3	1,5	-1,7

Tab. SI 7 Mean concentration of organic micropollutants during phase I and II in all sampling points.

	Centrate Feed,		MBR Permeate,		ED Concentrate,	
	µg/L		µg/L		µg/L	
	Phase I	Phase II	Phase I	Phase II	Phase I	Phase II
<b>4-Acetoaminoantipyrine</b>	12.45±4.5	10.13±0.9	3.21±1.4	2.23±1.4	<LOD	<LOD
<b>4/5-Methylbenzotriazole</b>	39.31±21.8	4.29±0.2	2.74±10	2.19±2.1	1.13±1.9	0.8±0.4
<b>Acesulfame</b>	10.14±4.3	4.52±2.4	0.15±0.6	1.2±0.6	0.3±0.7	0.95±0.5
<b>Acetaminophen</b>	<LOD	1.18±1.6	<LOD	<LOD	<LOD	<LOD
<b>Acetylsulfamethoxazole</b>	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
<b>Benzotriazole</b>	128.93±72	8.46±0.9	2.81±15.3	4.96±3	2.66±9.7	2.07±1
<b>Candesartan</b>	NA	NA	NA	14.04±0.6	<LOD	<LOD
<b>Carbamazepine</b>	7.2±3.5	5.04±0.7	1.88±3.7	5.43±2.6	0.06±0	1.58±0.7
<b>Diclofenac</b>	12.03±5.2	7.31±2.1	1.82±1.4	1.85±0.9	0.04±0.1	0.83±1.5
<b>Ep-Carbamazepine</b>	0.27±0.9	<LOD	1.34±0.7	2.35±2	<LOD	<LOD
<b>Gabapentin</b>	9.17±4.7	8.73±0.8	4.06±5.4	5.03±1.5	0.38±0.7	1.3±1.1
<b>Gabapentin-Lactam</b>	1.13±0.6	2.05±0.3	1.22±0.8	2.49±1.6	0.12±0.1	<LOD
<b>Hydrochlorothiazide</b>	n.d.	<LOD	n.d.	0.36±0.7	n.d.	<LOD
<b>Ibuprofen</b>	25.48±11.1	14.39±1.9	<LOD	<LOD	<LOD	<LOD
<b>Lamotrigine</b>	4.59±1.3	4.68±1.1	2.46±1.3	5.32±1.2	0.5±0.5	1.21±1.3
<b>Lidocaine</b>	0.89±0.5	0.8±0.1	0.6±0.4	0.79±0.4	0.59±0.3	2.34±1.6
<b>Metformin</b>	1.09±0.5	<LOD	<LOD	<LOD	1.27±0.3	5.78±2.2
<b>Metoprolol</b>	11.59±2.8	9.1±0.9	3.98±1.8	3.76±2.2	1±0.7	4.64±2.3
<b>Metoprolol Acid</b>	12.42±2.4	11.46±1.4	1.1±1.1	0.94±1.1	0.3±0.2	<LOD
<b>Oxipurinol</b>	4.03±176.4	2.81±1.9	<LOD	4.54±1.7	<LOD	0.19±0.6
<b>Sulfamethoxazole</b>	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
<b>Tramadol</b>	2.4±1	2.27±0.1	2.01±0.9	2.57±2.3	<LOD	<LOD

<b>Valsartan</b>	33.99±5.7	12.69±0.6	0.95±0.8	0.98±0.4	<LOD	<LOD
<b>Valsartan Acid</b>	1.23±0.1	1.7±0.6	11.19±2.2	17.12±9.3	13.75±1.9	6.45±4.4
<b>tDiOH-Carbamazepine</b>	2.12±0.4	2.38±0.5	1.59±0.4	3.4±1.6	<LOD	<LOD

*Tab.SI 8: Median concentration of nitrogen species in the MBR permeate.*

	<b>Phase I</b>	<b>Phase II</b>
<b>NH<sub>4</sub>-N [mg/L]</b>	4.2±2.9	0.8±0.5
<b>NO<sub>2</sub>-N [mg/L]</b>	1.0±1.0	0.1±0.0
<b>NO<sub>3</sub>-N [mg/L]</b>	863.2±54.0	798.7±100.3
<b>TN [mg/L]</b>	897.3±61.4	673.5±51.2



Tab. SI 9: Mean elimination of organic micropollutants over entire study period including phase I and phase II. Column “Retention ED” refers to elimination calculated for two-stage system using initial centrate load as reference. Retention “ED (stand-alone)” refers to elimination calculated considering the MBR permeate loads as reference.

	<b>Elimination MBR</b>	<b>Retention ED</b>	<b>Total Elimination</b>	<b>Retention ED (stand- alone)</b>
<b>4- Acetoaminoantipyrine</b>	69±9%	31±9.0%	100±13%	100±0.0%
<b>4/5- Methylbenzotriazole</b>	33±50%	64±47.0%	97±69%	95±3.0%
<b>Acesulfame</b>	86±13%	5±14.0%	91±19%	38±100.0%
<b>Acetaminophen</b>	100%	0%	100%	89%
<b>Acetylsulfamethoxazole</b>	-	-	-	-
<b>Benzotriazole</b>	49±45%	46±41.0%	95±61%	91±3.0%
<b>Carbamazepine</b>	-27±52%	98±4.0%	98±4%	98±4.0%
<b>Diclofenac</b>	77±6%	22±6.0%	99±8%	94±9.0%
<b>Ep-Carbamazepine</b>	-60±126%	100±0.0%	100%	100±0.0%
<b>Gabapentin</b>	37±15%	59±15.0%	96±21%	94±7.0%
<b>Gabapentin-Lactam</b>	-72±46%	99±2.0%	99±2%	99±2.0%
<b>Hydrochlorothiazide</b>	1%	99%	100%	100%
<b>Ibuprofen</b>	100%	-	-	-
<b>Lamotrigine</b>	-10±36%	97±3.0%	97±3%	97±3.0%
<b>Lidocaine</b>	-22±41%	74±21.0%	74±21%	74±21.0%
<b>Metformin</b>	76±48%	19±37.0%	95±61%	78±4.0%

<b>Metoprolol</b>	58±17%	38±16.0%	96±23%	90±11.0%
<b>Metoprolol_Acid</b>	86±6%	13±6.0%	99±8%	98±3.0%
<b>Oxipurinol</b>	50±60%	47±56.0%	97±82%	93±8.0%
<b>Sulfamethoxazole</b>	-	-	-	-
<b>Tramadol</b>	-49±71%	98±2.0%	98±2%	98±2.0%
<b>Valsartan</b>	94±3%	6±3.0%	100±4%	100±0.0%
<b>Valsartan Acid</b>	-1 070±259%	83±6.0%	83±6%	83±6.0%
<b>tDiOH-Carbamazepine</b>	-22±54%	100±0.0%	100%	100±0.0%

# Figures

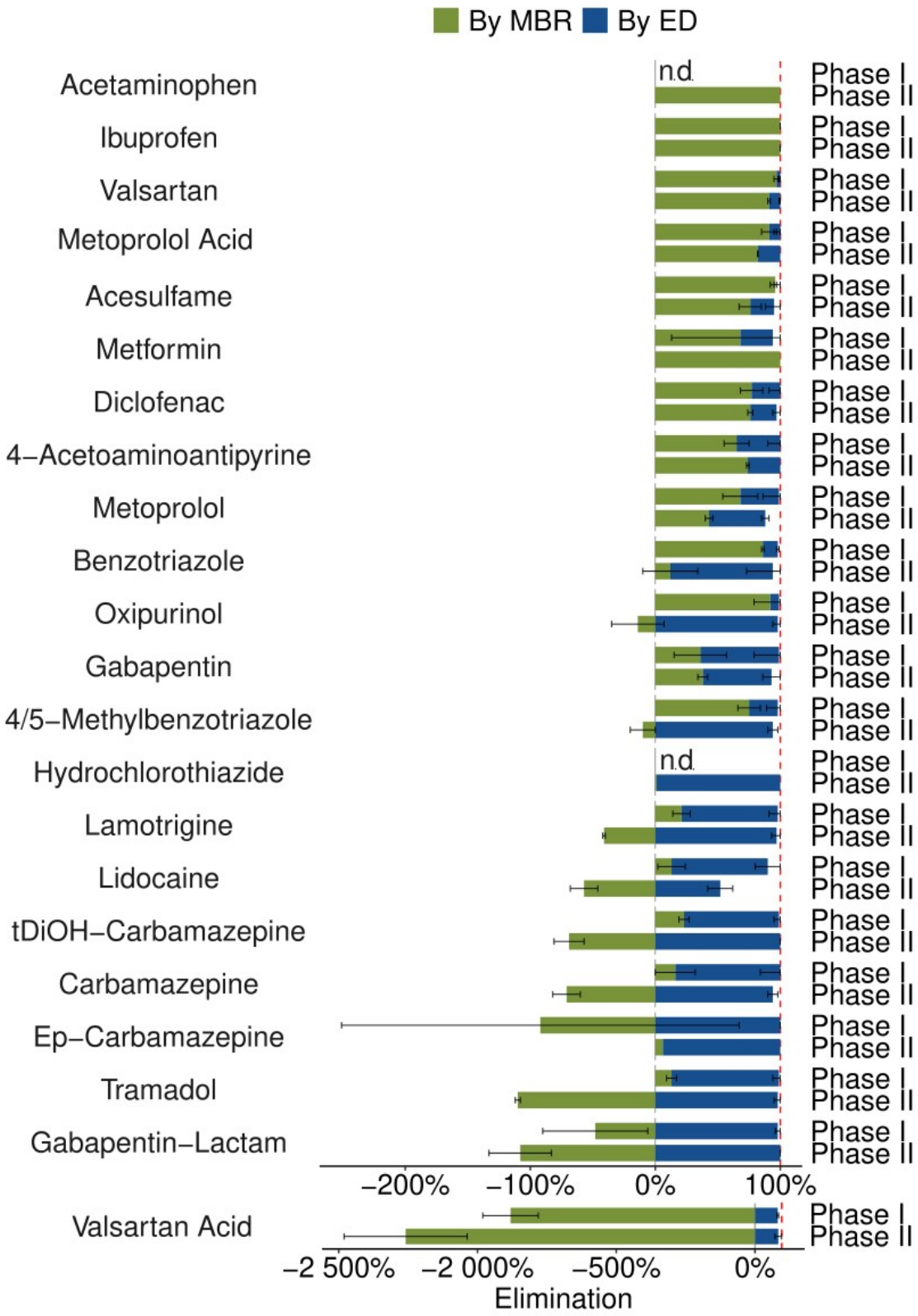


Fig. SI 1: Calculated elimination in the membrane bioreactor and the electro dialysis of organic micropollutants with strong differences between phase I and phase II for all investigated compounds. (n.d. for not determined)