Supplementary information:

Leaching Potential of Heavy Metals from Road-deposited Sediment and Sorptive Media during Dry Periods in Storm Water Quality Improvement Devices

Steffen H. Rommel [a], Luca Noceti [a], Philipp Stinshoff [a] and Brigitte Helmreich [a,*]

[a] Chair of Urban Water Systems Engineering, Technical University of Munich, Am Coulombwall 3, 85748 Garching, Germany; sww@tum.de

* Correspondence: b.helmreich@tum.de; Ph: +49-89-289-13719

Table S1 Physical characteristics of all materials before pre-stressing based on dry matter.

Parameter	d_{10}	d_{30}	d_{60}	Bulk density	Loss on ignition (550 °C)	Surface area (BET)	Total pore volume	CEC
Unit	mm	mm	mm	g L^{-1}	%	m^2 g-1	cm^3 g^{-1}	$cmol^+$ kg^{-1}
GAL	1.1	1.4	1.8	499	7.5	264.3	0.17	8.3
GFH	1.1	1.3	1.6	599	10.9	206.5	0.37	43.2
SED	0.004	0.012	0.055	781	16.3	2.4	-[a]	16.6
ZEO	0.7	1.1	1.6	915	6.2	31.2	0.07	23.0

[a] Determination of the total pore volume of SED was not possible due to the small particle size

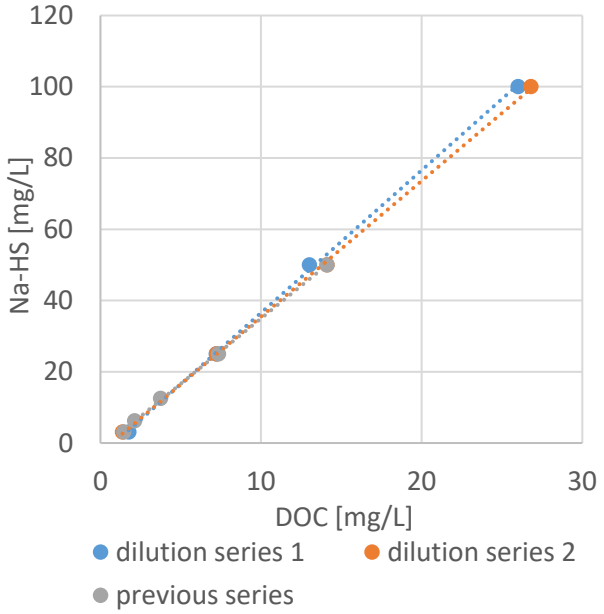

Fig. S1 Dilution-series of the used humic acid sodium salt (CAS-No. 68131-04-4; Carl Roth, Germany) in ultrapure water, linear regression of the data.

Pre-stressing of sorptive media

The target mass contents of Cu and Zn in the sorptive media after pre-stressing were determined following equation S1 and S2,

$$w_{m,Cu} = 5\ CEC_m M_{Cu} \cdot 0.106\ x_{CEC} \quad \text{(S1)}$$

$$w_{m,Zn} = 5\ CEC_m M_{Zn} \cdot 0.894\ x_{CEC} \quad \text{(S2)}$$

where $w_{m,i}$ is the mass content of the metal i (Cu or Zn) in media m (mg kg^{-1}), CEC_m is the cationic exchange capacity of media m ($cmol^+$ kg^{-1}), M_i is the molar mass of metal i (g mol^{-1}) and x_{CEC} is the target pre-stressing level defined as fraction of CEC_m. The target contents of Cu and Zn after pre-stressing are summarized in table S2.

Table S2 Target Cu and Zn content for the pre-stressing of the sorptive media

Experiment	Sorptive filter media					
	ZEO		GFH		GAL	
	Cu [g kg^{-1}]	Zn [g kg^{-1}]	Cu [g kg^{-1}]	Zn [g kg^{-1}]	Cu [g kg^{-1}]	Zn [g kg^{-1}]
10% CEC	0.075	0.675	0.141	1.268	0.027	0.244
40% CEC	0.301	2.699	-*	-*	-*	-*
60% CEC	0.452	4.048	-*	-*	-*	-*
80% CEC	0.602	5.398	-*	-*	-*	-*

* Experiments with 40, 60 and 80% CEC were only conducted with the media ZEO

Cleaning procedure of glass ware

1. Clean with DI water and a brush
2. Flush with DI water
3. Flush with acetone
4. Flush with DI water
5. Fill container with 0.1 M HNO_3 and let it rest for 24 h, dispose solution afterwards
6. Flush with DI water

Microwave-assisted hydrofluoric acid digestion method

1. Approximately 200 mg of sample was digested using 8 mL 65% nitric acid, 2 mL 40% hydrofluoric acid (s.p.) and 1 mL 30% hydrogen peroxide (s.p.) in a microwave digestion system (Mars 6, CEM, USA) at 200 °C.
2. Temperature was increased to 200 °C within 15 min. The temperature remained at 200 °C for 20 min. Afterwards it was cooled down for 20 min.
3. Subsequently, 1 mL hydrofluoric acid and 10 mL 4% boric acid were added and a second digestion at 180 °C was conducted. Excessive hydrofluoric acid was masked.
4. The digested solution was transferred quantitatively in a 250 mL volumetric flask and filled up with ultrapure water.
5. Afterwards, a 10 times diluted sample was analyzed using ICP-OES or ICP-MS.

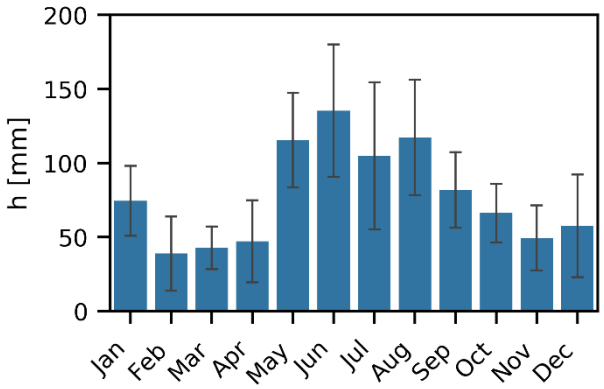

Fig. S2 Monthly precipitation height observed in Munich, Germany, at weather station 3379 of the Deutscher Wetterdienst. Data of the years 2010–2018 is shown, bar heights indicate mean values, the error bars denotes the SD.

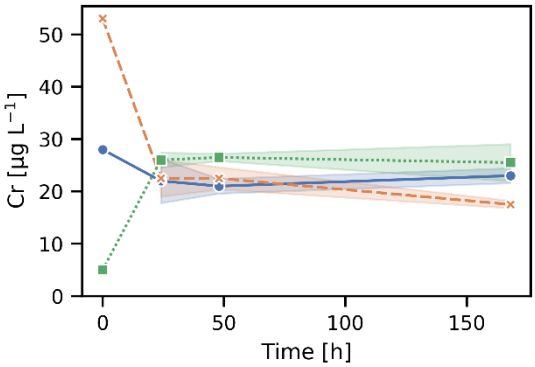

Fig. S3 Time-series of dissolved Cr in the leachates of SED the different media and SRRs. Shown is the mean of two replicates. The shaded area denotes the SD.

Modeling of leaching behavior

Degaffe and Turner (2011) modeled the leaching behavior of Zn from tire wear particles with a diffusion-controlled leaching model following equation S3,

$$[\mathrm{Me}] = \mathrm{kt}^{1/2} \quad \text{(S3)}$$

where [Me] represents dissolved metal concentrations at time t. The parameter k (µg L^{-1} $h^{-0.5}$) is the rate constant of the diffusion-controlled leaching process (Degaffe and Turner, 2011).

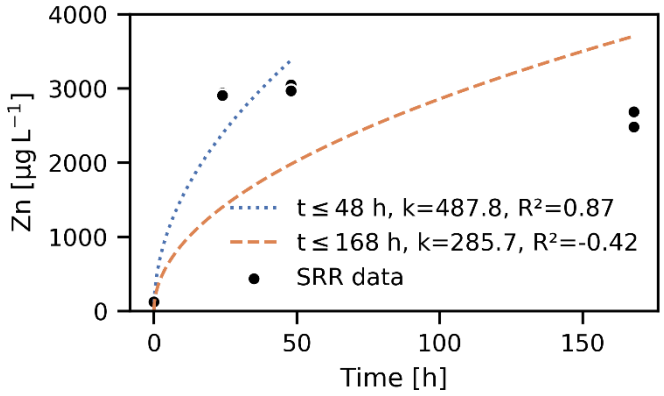

Fig. S4 Time-series of dissolved Zn in the SRR leachates of SED. Dotted and dashed line showed the diffusion-controlled fitted for t≤48 h data and all data, respectively.

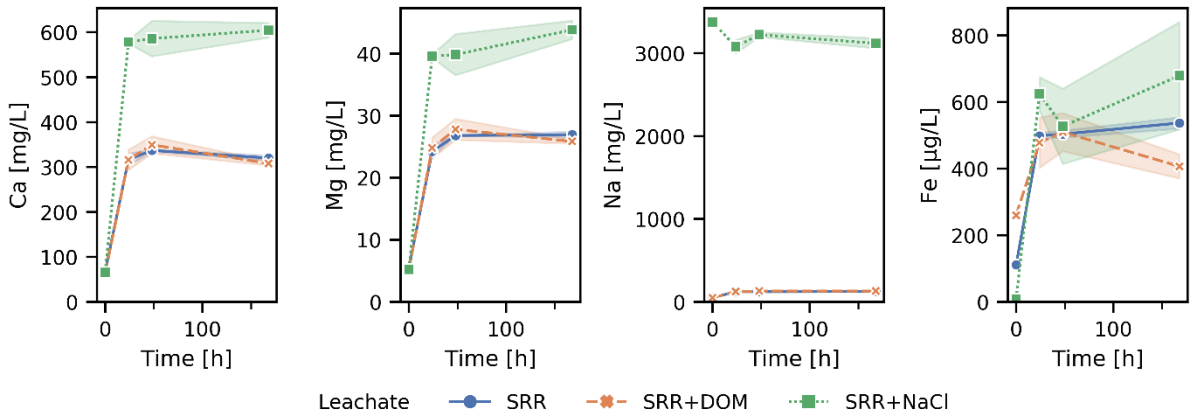

Fig. S5 Time-series of dissolved Ca, Mg, Na and Fe in the leachates of SED the different media and SRRs. Shown is the mean of two replicates. The shaded area denotes the SD.

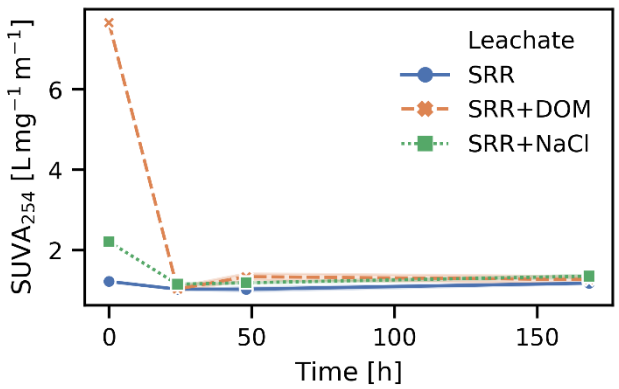

Fig. S6 Time-series of $SUVA_{254}$ in the leachates of SED. Shown is the mean of two replicates. The shaded area denotes the SD.

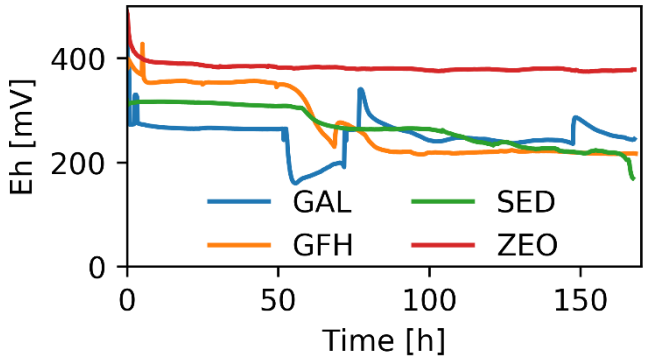

Fig. S7 Time-series of the ORP relative to the standard hydrogen electrode (Eh)in the SRR+DOM leachates of GAL, GFH, ZEO (all 10% pre-stressed) and SED

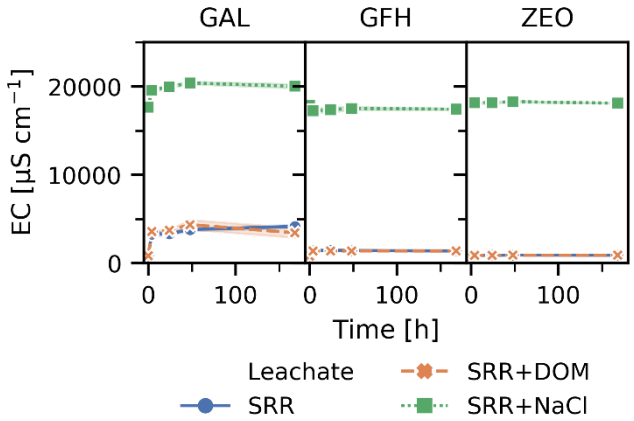

Fig. S8 Time-series of EC in the leachates of the different media and SRRs. Shown is the mean of two replicates. The shaded area denotes the SD.

Table S3 Speciation of SRRs predicted by Visual MINTEQ, species with fractions <1% were removed.

SRR		SRR+NaCl		SRR+DOM	
77.7	$CuCO_3$ (aq)	68.1	$CuCO_3$ (aq)	96.0	HA2-Cu(6)(aq)
13.0	$CuOH^+$	13.5	Cu^{2+}	4.0	HA1-Cu(6)(aq)
5.9	Cu^{2+}	13.5	$CuOH^+$		
2.0	$Cu(OH)_2$ (aq)	1.6	$Cu(CO_3)_2^{2-}$		
1.0	$Cu(CO_3)_2^{2-}$	1.5	$CuCl^+$		
		1.3	$Cu(OH)_2$ (aq)		
75.6	Zn^{2+}	77.5	Zn^{2+}	50.2	HA2-Zn(6)(aq)
9.8	$ZnCO_3$ (aq)	12.0	$ZnCl^+$	23.3	Zn^{2+}
5.7	$Zn(OH)_2$ (aq)	3.8	$ZnCO_3$ (aq)	18.0	HA1-Zn(6)(aq)
5.3	$ZnOH^+$	2.5	$ZnOH^+$	3.1	$ZnCO_3$ (aq)
1.4	$ZnSO_4$ (aq)	1.7	$Zn(OH)_2$ (aq)	2.0	$Zn(OH)_2$ (aq)
1.4	$ZnHCO_3^+$	1.1	$ZnCl_2$ (aq)	1.8	$ZnOH^+$

References

Degaffe, F.S., Turner, A., 2011. Leaching of zinc from tire wear particles under simulated estuarine conditions. Chemosphere 85, 738–743. https://doi.org/10.1016/j.chemosphere.2011.06.047