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Supplementary material

Contaminant release from aged microplastic

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Table S1. Comparison of the duration for artificial weathering and the equivalent in outdoor weathering based on equal UV exposure

Duration of artificial exposure in weathering device [h]	UV radiant exposure [MJ/m^2]	UV equivalent duration for outdoor exposure in Central Europe
1000	90	2 months
2000	180	4 months

Table S2. Temperature program micro wave digestion

Plastic type	Heating rate [°C/min]	Final temperature [°C]	Hold time [min]	Heating power [W]
PS	34	120	–	700
	40	200	–	800
	67	235	18	800
HDPE	31	110	–	700
	19	215	–	800
	0	215	20	1000
PVC	28	110	–	700
	26	210	–	800
	0	210	13	1000

Table S3. Limit of Detection (LOD), precision and accuracy of analytical methods

Analyte	LOD[A] [mg/L]	RSD [%][b] n=3	Accuracy [%][c]
Al	0.0360	6.00	106.4
Ba	0.0006	1.10	99.4
Ca	0.1080	1.10	98,5
Cd	0.0004	0.75	100.6
Co	0.0003	0.60	101.4
Cr	0.0004	1.20	102.7
Cu	0.0040	2.00	99.3
K	0.3720	4.00	96.4
Mg	0.0340	0.60	100.1
Mn	0.0000	0.80	100.6
Mo	0.0004	4.70	97.3
Na	0.3980	1.30	99.3
Pb	0.0034	1.60	102.7
Sr	0.0003	3.00	99.0
V	0.0013	1.10	98.4
Zn	0.0090	3.50	102.4

[A]LOD: aqueous samples acidified with HNO_3 and measured using ICP-OES; [b] aquous samples acidified with HNO_3, highest RSD observed is stated; [c]aqueous standard was used as control sample and recovery was calculated using the linear regression of the calibration curve.

Evaluation recovery functions

The aim of recovery determination of an analytical method is the determination of the influence of the matrix on the results. We evaluated the influence of the digestion using different mixtures of nitric acid and hydrogen peroxide on the analytical results. The standard calibration using aqueous standards acidified with nitric acid serves as basis for comparison. This calibration curve can be described by the following equation:

$$y = a_c + b_c \times x_c \qquad \text{(S1)}$$

where y = peak area of detector signal; a_c = intercept calibration curve; b_c = slope calibration curve and x_c = concentration standards.

Equation S1 can be rearranged to:

$$x_c = \frac{y_c - a_c}{b_c} \qquad \text{(S2)}$$

In the next step every standard is analysed using the modified analytical method. The detector signal of the modified method y_f is transferred to concentrations x_f using the standard calibration.

$$x_f = \frac{y_f - a_c}{b_c} \qquad \text{(S3)}$$

x_f is plotted against x_c to derive the recovery function which can be described by:

$$x_f = a_f + b_f \times x_c \qquad \text{(S4)}$$

The regression line of the recovery function has ideally a slope of 1 and an intercept of 0. Comparison is only possible if the standard deviation for the procedure (S_{xoc}) and the residual standard deviation (S_{yf}) of recovery function are comparable. They are calculated according to the following equations:

$$s_y = \sqrt{\frac{\sum[\hat{y}_i - y_i]^2}{N_f - 2}} \qquad \text{(S5)}$$

$$s_{yf} = \sqrt{\frac{\sum\left[\hat{y}_{if} - y_{if}\right]^2}{N_f - 2}} \qquad \text{(S6)}$$

where N_f = number of calibration levels, 6; $\hat{y}_i$ = signal calculated using the regression of calibration of standard method; $\hat{y}_{if}$ = signal calculated using the regression of recovery function

$$S_{xoc} = \frac{s_y}{b_c} \qquad \text{(S7)}$$

The following limit value (LV) is calculated and used for the F-test of equality of variances:

$$LV = \left(\frac{s_{yf}}{s_{xoc}}\right)^2 \qquad \text{(S8)}$$

LV is compared with the critical value of the F-distribution (α=0.01, f_1, f_2). The degrees of freedom (f_1 and f_2) equals $N_f - 2 = 4$. The difference in variance are significant if LV > F (α = 0.10; $f_1 = f_2 = 4$). The limit value is 15.98 in our case. For all analytes, the difference in variance is not significant and the recovery functions can be used to evaluate the influence of the matrix. As usually the slope and intercept differ from the ideal values of 1 and 0 confidence intervals for both are calculated.

$$CI(a_f) = a_f \pm t_{pf} \times s_{yf} \times \sqrt{\frac{1}{N_f} + \frac{\bar{x}_c^2}{Q_{xx}}} \qquad \text{(S9)}$$

$$CI\ (b_b) = b_f \pm \frac{t_{P,t} \times s_{y,f}}{\sqrt{Q_{xx}}} \qquad \text{(S10)}$$

where $t_{p,f}$ = students t-faktor: P = 95%; f = $N_f - 2 = 4$); Q_{xx}: sum of squares.

Table S4. Confidence intervals (CI) for intercept (a_f) and slope (b_f) of recovery functions of digestion mixtures

CI (a_f) not including 0 and CI (b_f) not including 1 are marked in red.

	Acidic mixture used for PS digestion		Acidic mixture used for PVC digestion	
Analyte	CI (a_f)	CI (b_f)	CI (a_f)	CI (b_f)
Al	–0.316/1.844	0.955/1.113	–0.131–3.854	0.885–1.177
Ba	–0.048/0.058	0.956/1.091	–0.032–0.048	0.949–1.050
Ca	–0.299/0.147	0.996/1.029	–0.718–0.314	0.988–1.066
Cd	–0.016/0.032	0.979/1.040	–0.012–0.016	0.989–1.024
Co	–0.019/0.037	0.969/1.039	–0.005/0.014	0.992/1.016
Cr	–0.022/0.036	0.973/1.047	–0.021/0.060	0.943/1.046
Cu	–0.033/0.040	0.969/1.061	–0.024/0.033	0.968/1.040
K	–0.654/0.103	0.988/1.043	–0.443/1.168	0.953/1.071
Mg	–0.089/0.372	0.996/1.030	–0.149/–1.275	1.007/1.0089
Mn	–0.009/0.026	0.990/1.034	–0.011/0.026	0.978/1.024
Mo	–0.027/0.050	0.962/1.059	–0.039/0.057	0.954/1.075
Na	–0.552/–0.183	0.988/1.034	–0.397/-1.429	1.000/1.075
Pb	–0.019/0.030	0.983/1.044	–0.003/0.003	1.006/1.014
Sr	–0.027/0.047	0.942/1.035	–0.029/0.052	0.943/1.044
V	–0.003/0.017	0.996/1.022	–0.020/0.031	0.977/1.042
Zn	–0.012/0.030	0.981/1.035	–0.006/0.021	0.985/1.020

If the confidence intervals do not include $a_f = 0$ and $b_f = 1$ it can be concluded acidic matrix of the digestion significant differences. Table S4 shows that for most analytes this is not the case. Exceptions are Pb, Mg and Na.

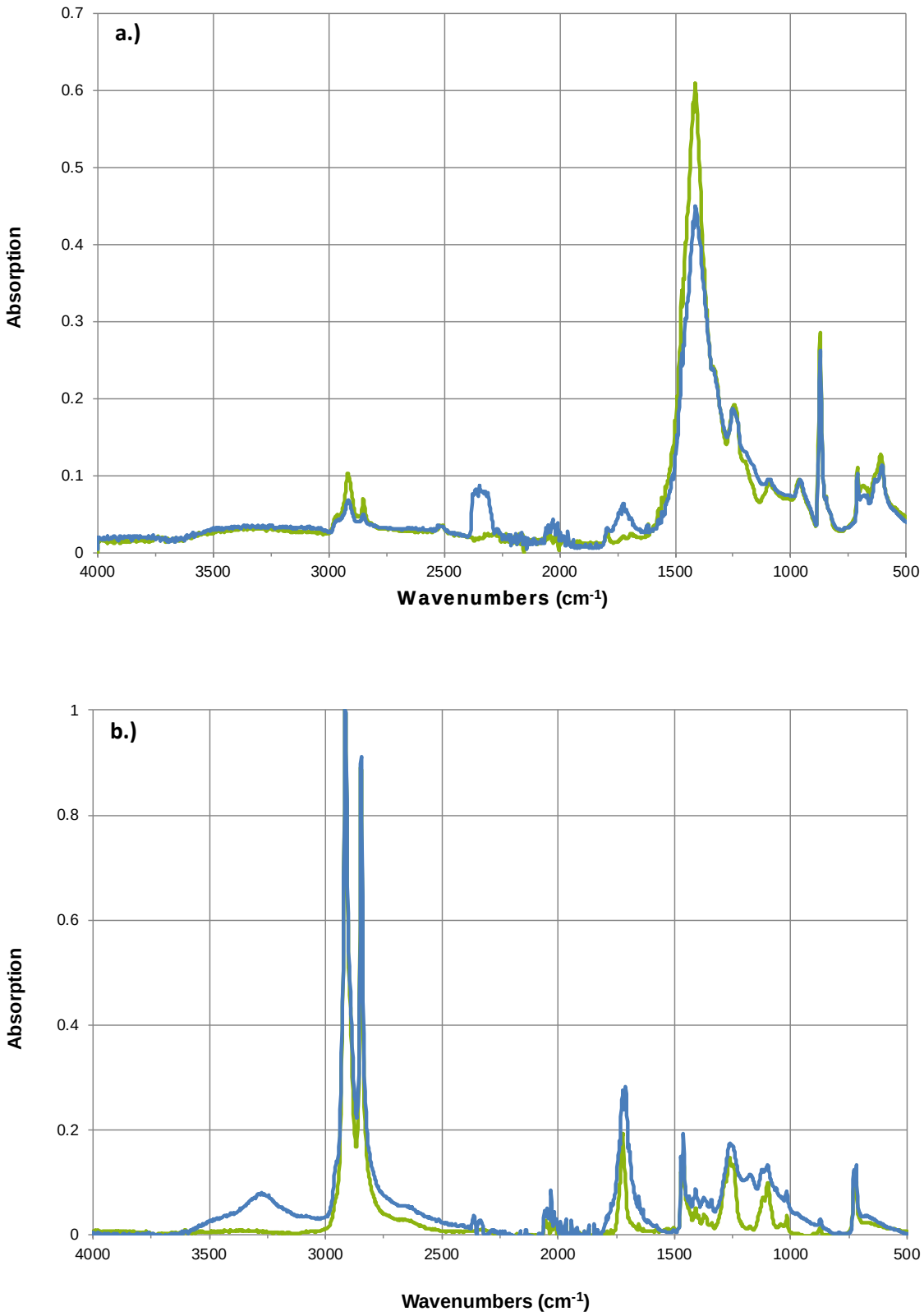

Fig. S1. ATR/IR spectra of a.) PVC and b.) HDPE unexposed (green) and exposed 1000 h UV (blue).

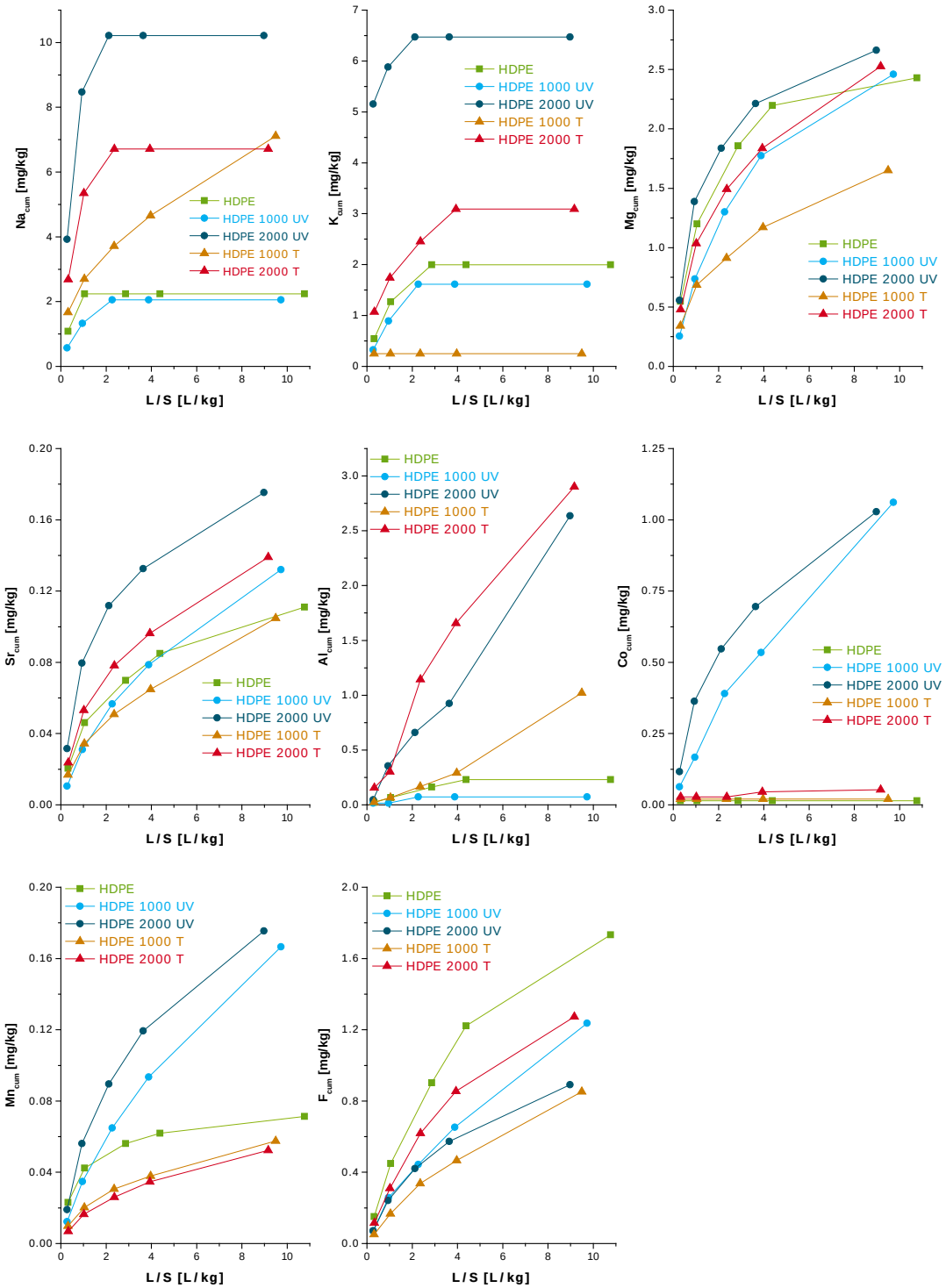

Fig. S2. Cumulative release of metal ions (Na, K, Mg, Sr, Al, Co and Mn) in column leaching experiments with unexposed (green symbols and lines) and aged samples of HDPE (red/orange: thermo/oxidative, dark blue/bright blue: thermo/ and photo/oxidative).

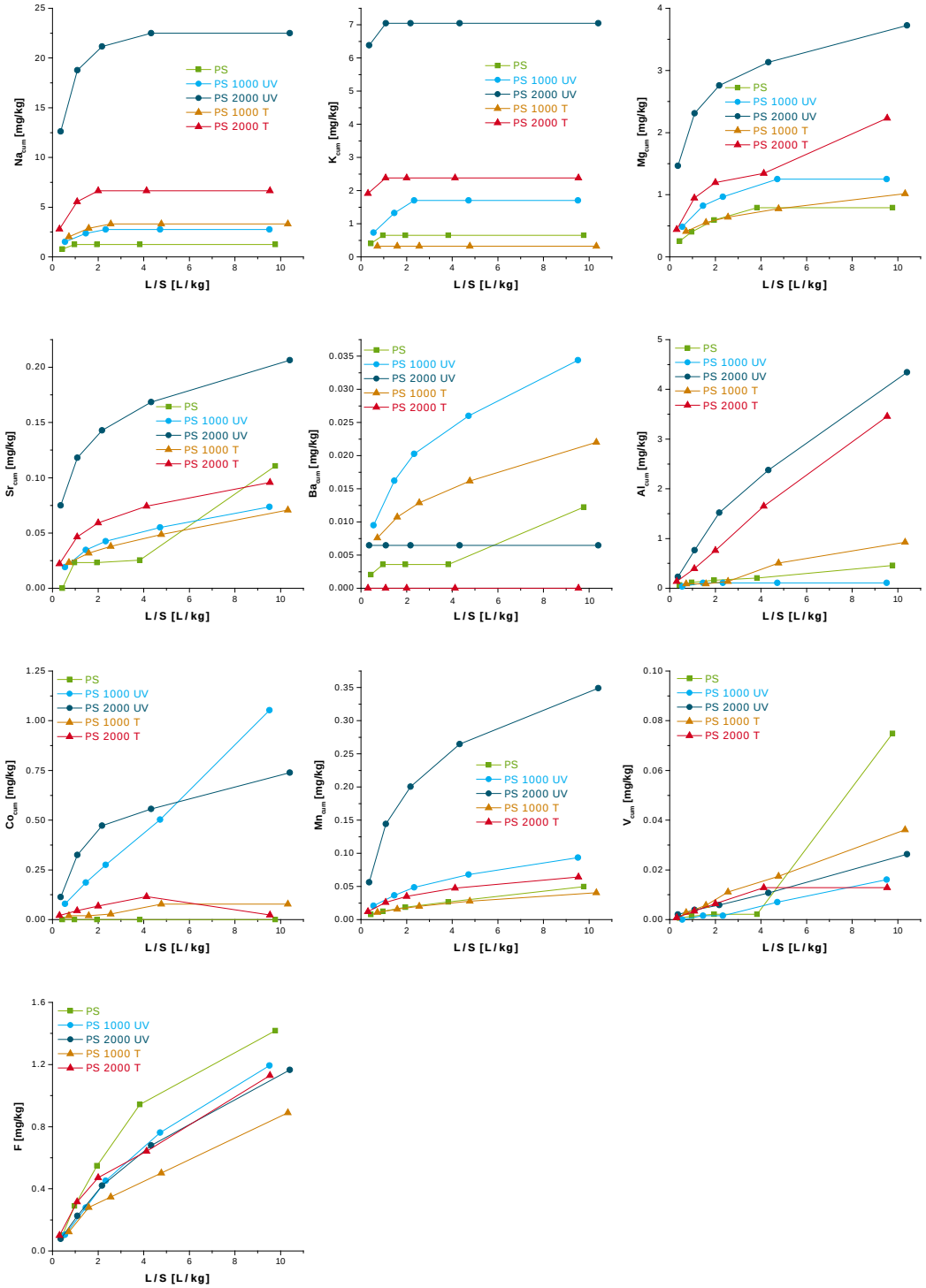

Fig. S3. Cumulative release of metal ions (Na, K, Mg, Sr, Ba, Al, Co and Mn) in column leaching experiments with unexposed (green symbols and lines) and aged samples of PS (red/orange: thermo/oxidative, dark blue/bright blue: thermo/ and photo/oxidative).

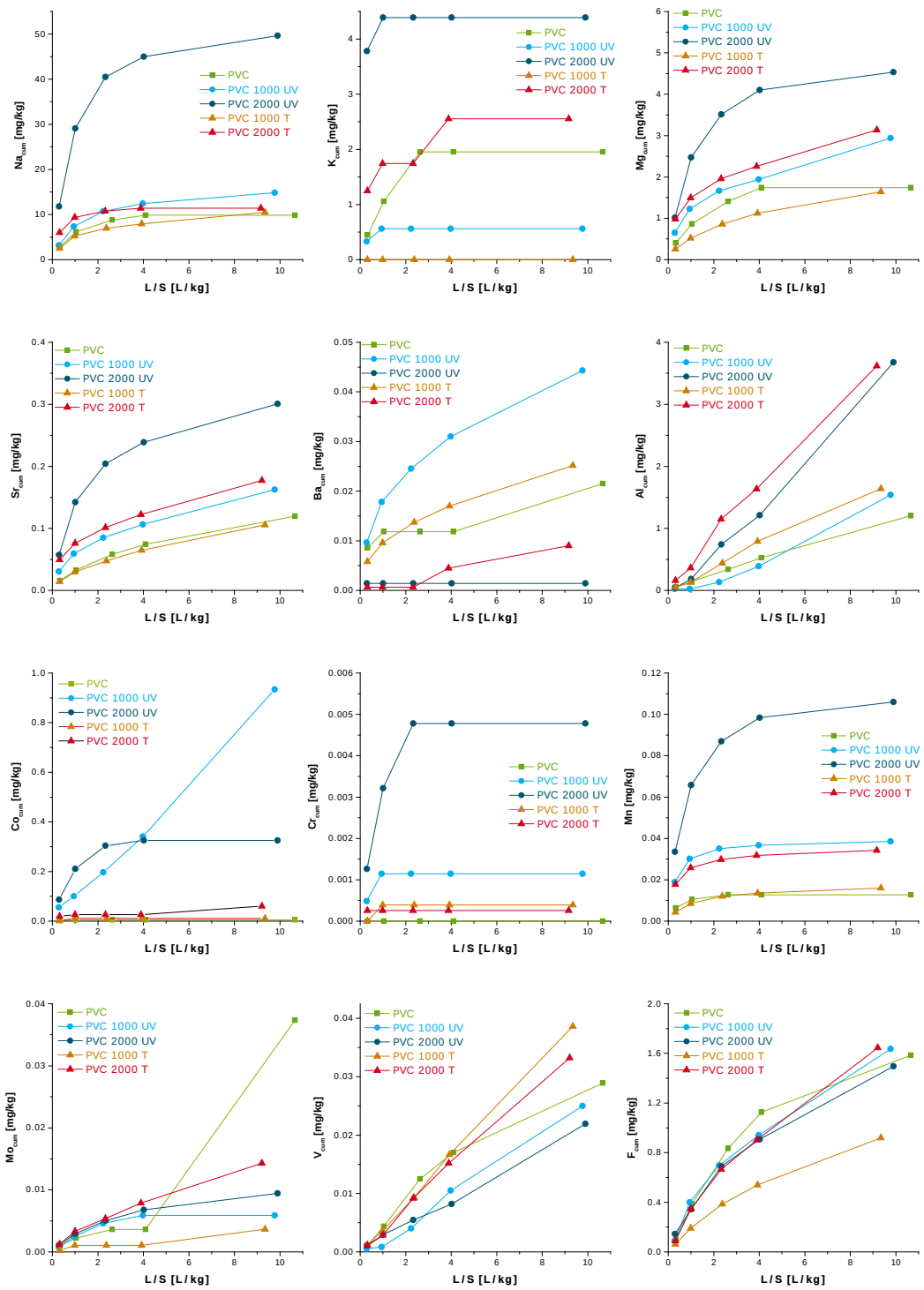

Fig. S4. Cumulative release of metal ions (Na, K, Mg, Sr, Ba, Al, Co, Mo, Mn and Cr) in column leaching experiments with unexposed (green symbols and lines) and aged samples of PVC (red/orange: thermo/oxidative, dark blue/bright blue: thermo/ and photo/oxidative).

Table S3. Information on biodegradation, GHS harzard statements concerning the environment and on the concentration inducing an effect for 50 % of the testorganism (EC50) for the substances tentatively identified in the eluates

Compound	Readily biodegradable		EC_{50} [mg/L]	Organism
styrene	yes	–	0.56[1]	*Pseudokirchneriella subcapitata*
			4.7[1]	*Daphnia magna*
			12[1]	*Pimephales promelas*
acetophenone	yes	–	42.77[2]	*Tetrahymena pyriformis*
1,2-diphenylethane-1,2-dione	n.d.	–	–	–
4-hydroxyacetophenone	yes	H412	64[3]	*Daphnia magna*
1,3-diphenylpropan-2-one	n.d.	–	0.00175[4]*	*Ceriodaphnia dubia*
5-ethyldihydro-2(3H)furanone	n.d.	–	8200[2]	*Tetrahymena pyriformis*
2,4-di-methylanilin	no	H411	5[5]	*Scenedesmus quadricauda*
5-pentyldihydro-2(3H)furanone	yes	–	152[2]	*Tetrahymena pyriformis*
5octyldihydro-2(3H)furanone	n.d.	–	–	–
5-heptyldihydro-2(3H)furanone	yes	H412	–	–
butylhydroxytoluene	yes	H410	1.7[6]	*Tetrahymena pyriformis*
di-n-butylphthalate (DBP)	yes	H400	3.7	*Daphnia magna*
d-(2-ethyl)phthalate (DEHP)	yes	–	0.41[7]	*Pseudokirchneriella subcapitata*
di-isoocylphthalate (DIOP)	no	H410	0.140	*Daphnia magna*
di-n-octylphthalate (DOP)	n.d.	–	–	–

*EC25; n.d. = no data

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