Potential human health risks of microplastic associated chemicals

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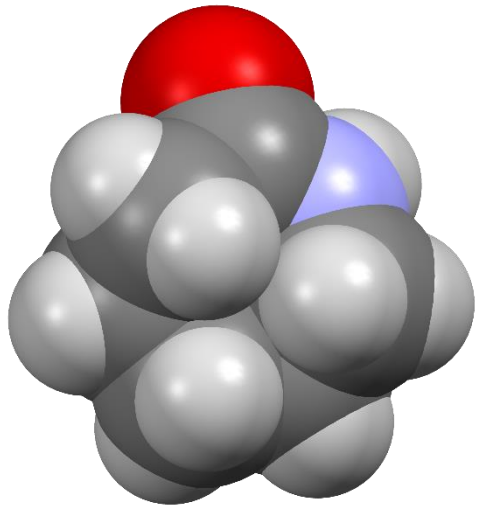
Microplastics and possible hazards for human health

- Global plastic production 320 million tons/year -> Environment -> UV, wind, waves, abrasion -> microplastics
- Microplastics < 5 mm
- Microplastics detected in food, drinking water and air

- Possible toxic effects of microplastic particles:
  - Plastic particle itself harmful
  - **Adsorbed (in)organic contaminants**
  - **Leaching of toxic additives**

- Which chemicals are present in microplastics?
- Are they released in the human intestines?
- Can we predict the intestinal uptake of chemicals?

From a chemical perspective microplastics contain....



Multiple additives:

- Plasticizers, flame retardants, stabilizers and pigments

Other chemicals:

- Unreacted monomers, starting substances and non-intentionally added substances (NIAS, impurities and side or breakdown products)

Environmental contaminants:

- Polychlorinated biphenyls, polycyclic aromatic hydrocarbons and many others

Microplastics in this study

Pristine plastics:

- Polyethylene (PE) cryomilled to 250 µm
- Polypropylene (PP) cryomilled to 250 µm
- Polyamide (PA) cryomilled to 250 µm
- Polystyrene (PS) cryomilled to 250 µm
- Polyvinyl chloride (PVC) cryomilled to 250 µm

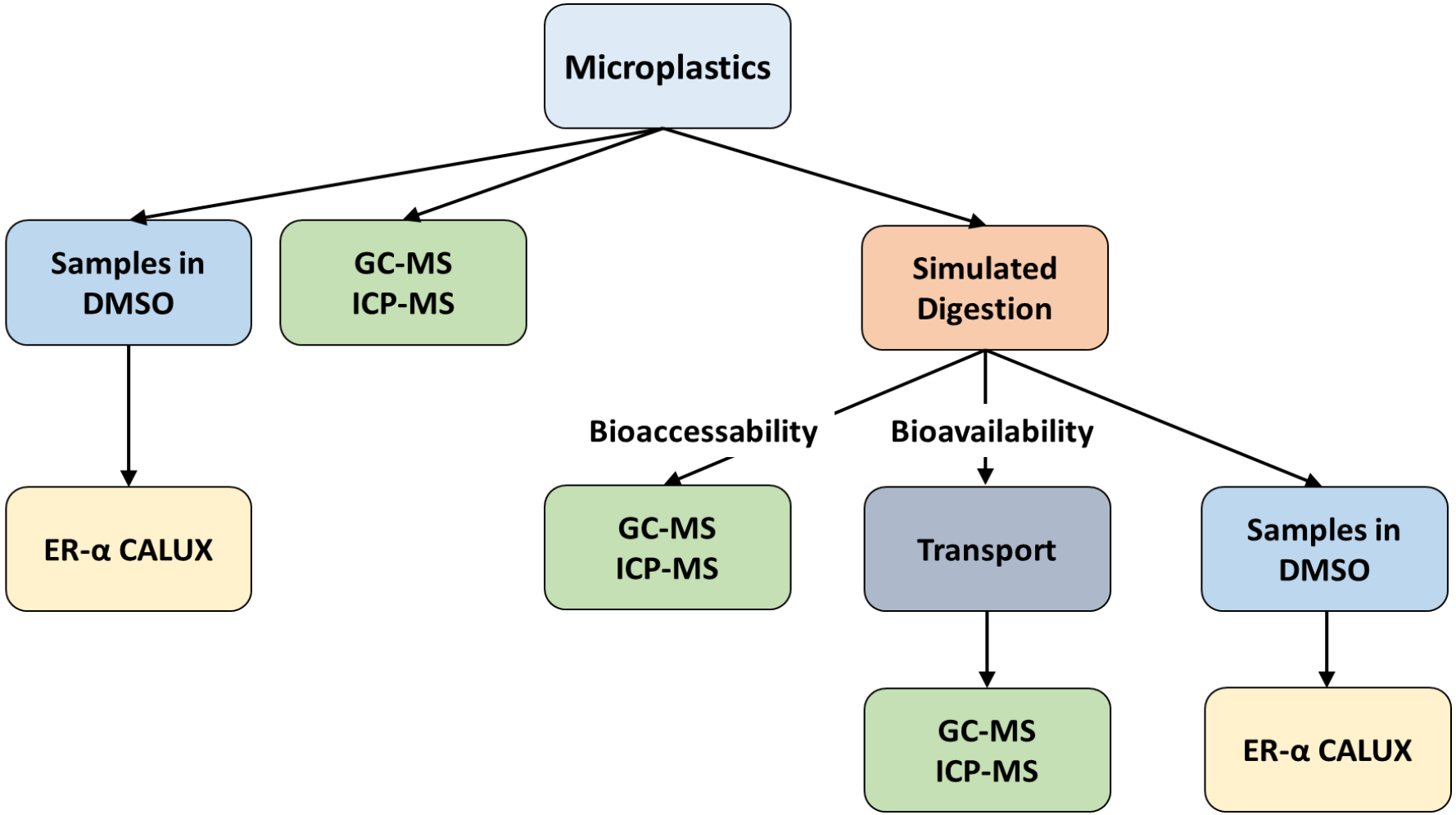
Plastics from food containers:

- Polypropylene (PP) from a food container cryomilled to 100 µm
- Polyethylene terephthalate (PET) from a bottle cryomilled to 100 µm

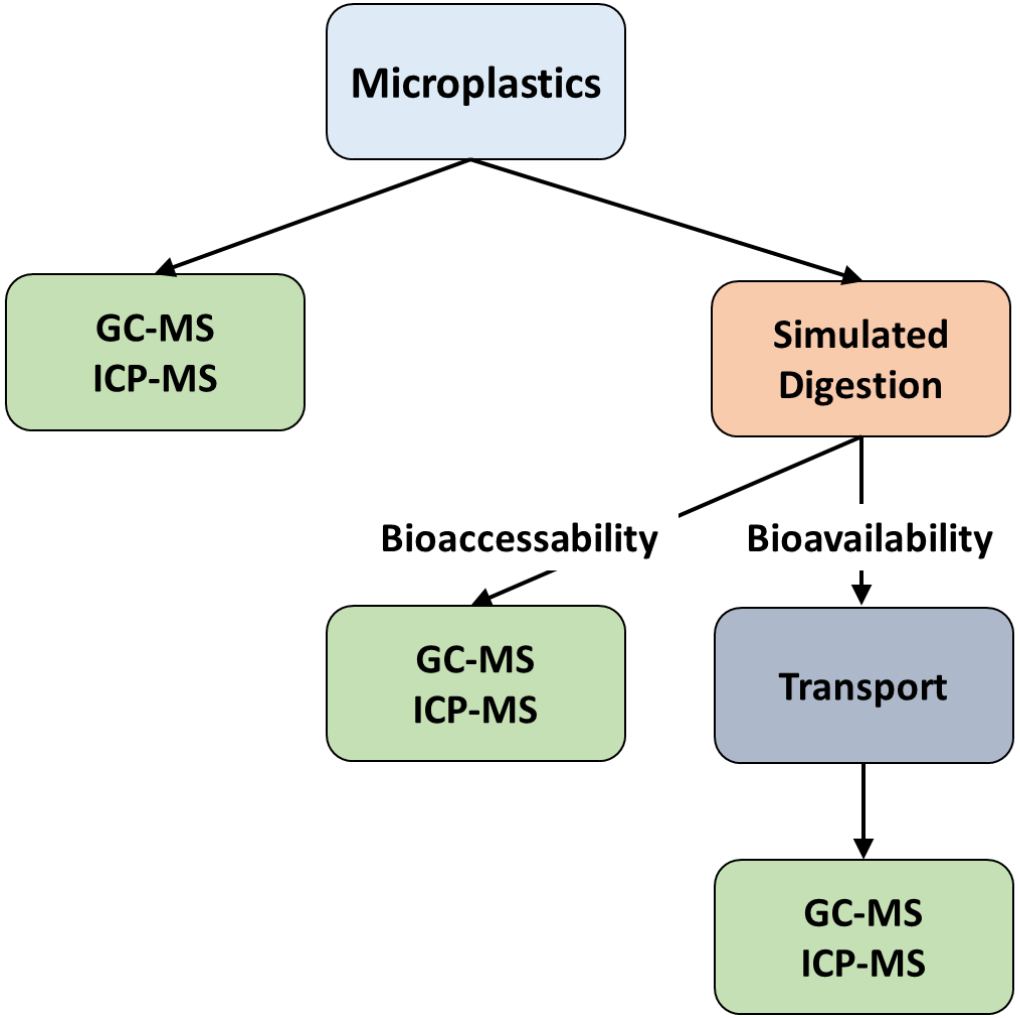
Environmentally relevant microplastics:

- Collected on Dutch beaches and cryomilled to sizes of 1 and 3 mm

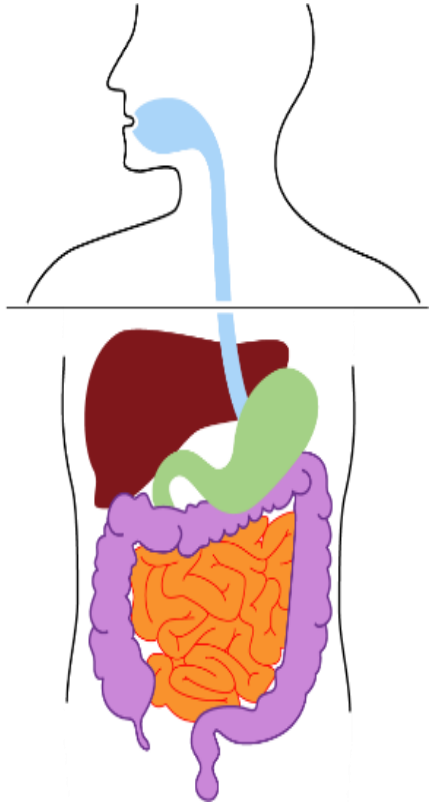
Experimental design of the study

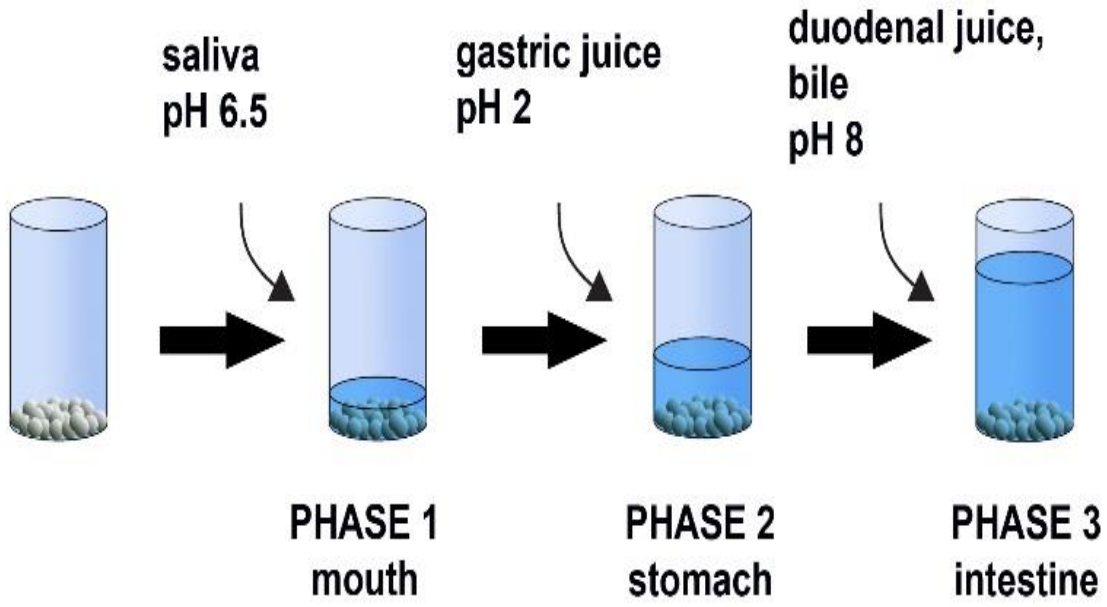


Experimental design of the study



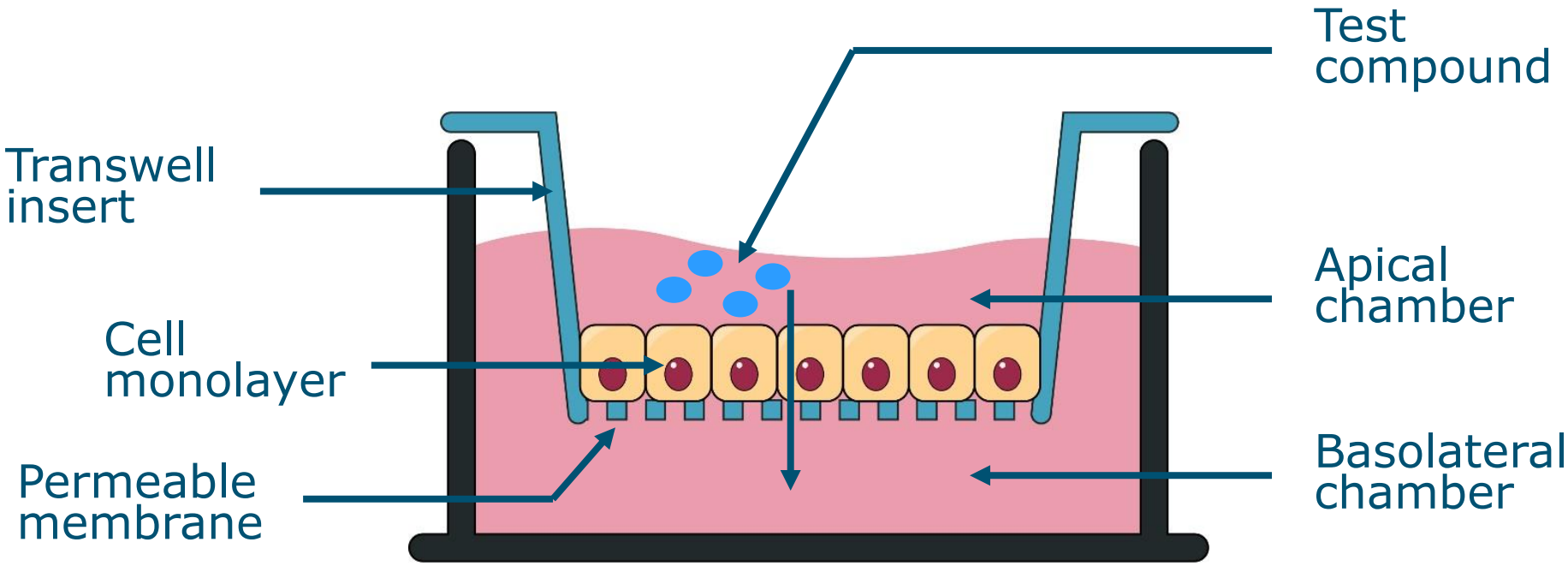
The *in vitro* human gastrointestinal digestion model



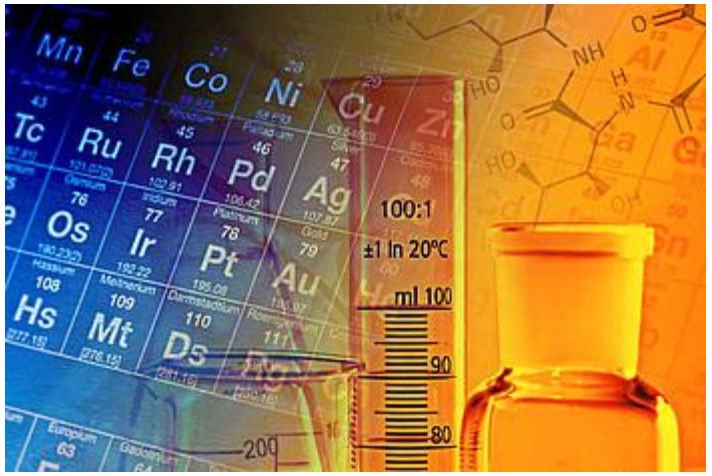


Pictures from Meike van der Zande

The *in vitro* human intestinal barrier model



Analysis of microplastics and leachates



Organic compounds:

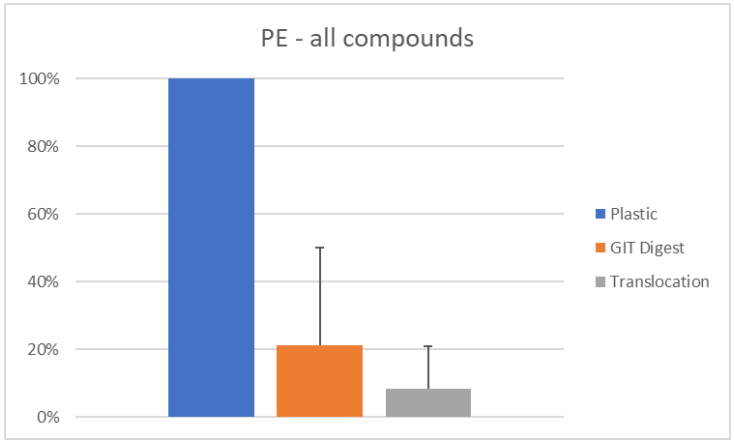
- Microplastics were ultrasonically extracted with ethyl acetate
- Leachates from in vitro human digestion and translocation experiment were extracted with ethyl acetate
- Extracts were analyzed with GCxGC/TOFMS
- Identification using a dedicated in-house MS database (650 compounds) and a NIST database
- Quantification based on external and internal standards

Elements:

- Microplastics were digested using conc. nitric acid and extracts diluted
- Leachates from in vitro human digestion and translocation experiment were acidified to 3% nitric acid
- Digests were analyzed with ICP/MS in the scanning mode
- Quantification based on external and internal standards

Overview of chemicals quantified in leachates from polyethylene MP

All compounds (mg/kg)



	PE		
	P	D	T
Tris(1-chloro-2-propyl)phosphate	0.2	0.2	0.1
Tris(2-chloropropyl)phosphate	0.1		
Bis(2-ethylhexyl) phthalate	4.2	0.8	0.3
Phthalic acid, di(oct-3-yl) ester	0.5	0.1	
1,15-Pentadecanediol	0.8	0.1	0.1
Fluorene	0.3		

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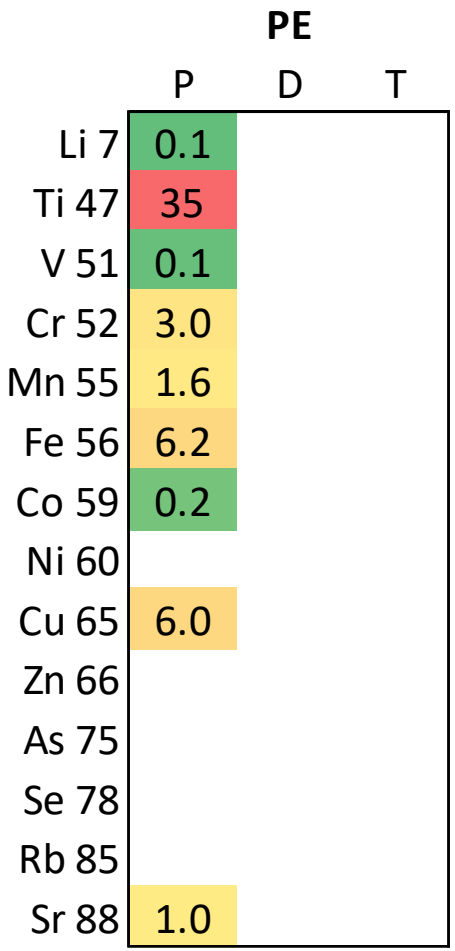
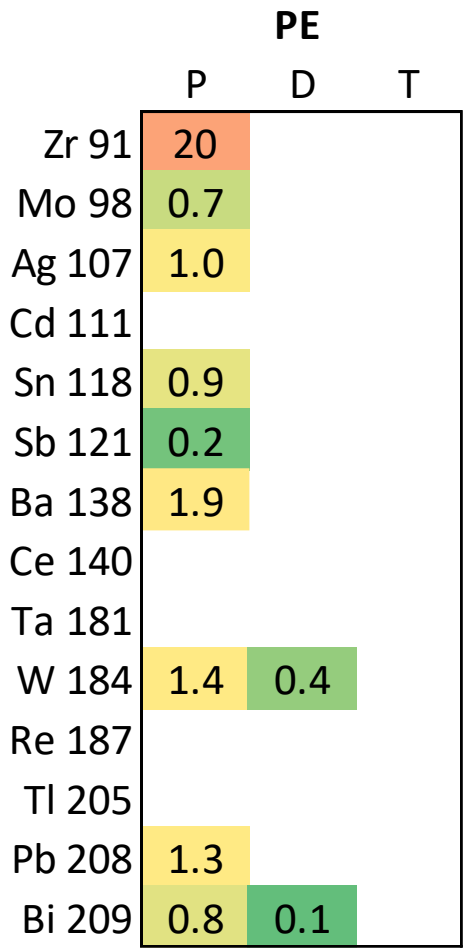
Overview of elements in plastics and leachates from polyethylene MP

Elements (mg/kg)





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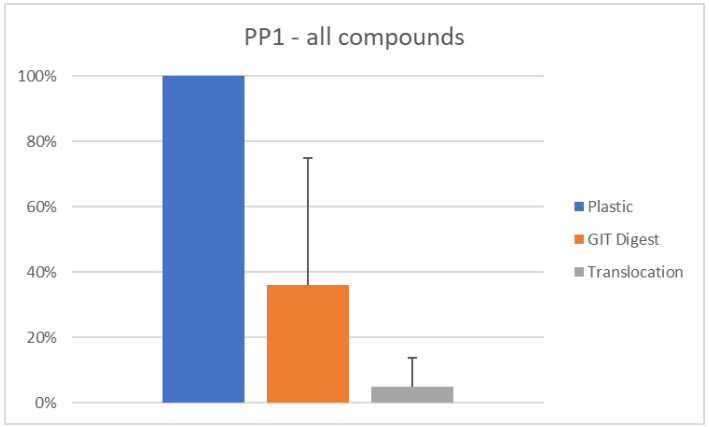
Overview of chemicals quantified in leachates from polypropylene MP

All compounds (mg/kg)



	PP-1		
	P	D	T
Tris(1-chloro-2-propyl)phosphate	0.3	0.3	
Tris(2-chloropropyl)phosphate	0.1		
Bis(2-ethylhexyl) phthalate	1.9	0.5	0.2
Dibutyl phthalate	0.2	0.1	
Phthalic acid, di(2-propylpentyl) ester	1.1	0.2	
Borane, diethyl(decyloxy)	0.8	0.1	
n-Hexadecanoic acid	2.1	2.6	0.5
Octadecanoic acid	7.6	5.4	1.2
Antracene	5.8	1.1	
Naphtalene	0.2		
Phenanthrene	4.8	1.0	

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Overview of elements in plastics and leachates from polypropylene MP

Elements (mg/kg)	PP-1			PP-1		
	P	D	T	P	D	T
Li 7	0.5			Zr 91	0.8	
Ti 47	2.0			Mo 98	0.1	
V 51	0.3			Ag 107		
Cr 52				Cd 111		
Mn 55	1.7			Sn 118		
Fe 56	116	4.7		Sb 121	0.1	
Co 59				Ba 138	16	
Ni 60				Ce 140	0.2	
Cu 65				Ta 181		
Zn 66				W 184		
As 75				Re 187	0.1	
Se 78				Tl 205		
Rb 85				Pb 208	0.5	
Sr 88	0.9			Bi 209		

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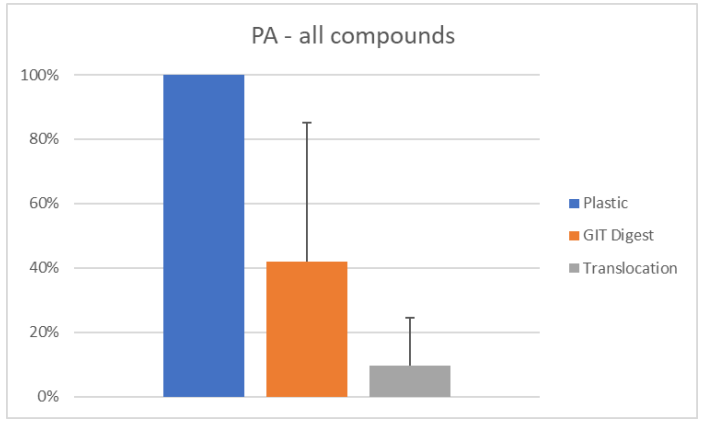
Overview of chemicals quantified in leachates from polyamide MP

All compounds (mg/kg)



	PA		
	P	D	T
Triisobutylphosphate	0.1		
Triphenylphosphate	0.1		
Tris(1-chloro-2-propyl)phosphate	0.3	0.1	
Tris(2-chloropropyl)phosphate	0.1		
Bis(2-ethylhexyl) phthalate	0.4	0.5	0.1
Dibutyl phthalate	0.2	0.1	
Phthalic acid, di(2-propylpentyl) ester	0.7	0.4	0.3
Phthalic acid, hept-4-yl isobutyl ester	0.6	0.4	0.1
1,8-Diazacyclotetradecane-2,9-dione (=nylon-6 cyclic oligomer)	42	1.0	
Caprolactam (=nylon-6 monomer)	70	46	25
Octadecane, 1-isocyanato-	5.3	0.1	
Tetrazolo[1,5-b]1,2,4-triazine, 5,6,7,8-tetrahydro-6,7-dimethyl-	2.6	2.9	

Overview of elements in plastics and leachates from polyamide MP

Elements (mg/kg)

	PA		
	P	D	T
Li 7	0.2		
Ti 47	10		
V 51	1.5	0.6	
Cr 52	7.4		
Mn 55	1.3		
Fe 56	5.2		
Co 59	0.3		
Ni 60			
Cu 65	5.2		
Zn 66			
As 75			
Se 78			
Rb 85			
Sr 88	1.9		

	PA		
	P	D	T
Zr 91	32		
Mo 98	1.3	0.7	
Ag 107	1.2		
Cd 111			
Sn 118			
Sb 121			
Ba 138	5.4		
Ce 140	0.5		
Ta 181	0.9		
W 184	5.3	0.7	
Re 187			
Tl 205	0.4		
Pb 208	1.4		
Bi 209	21	4.4	

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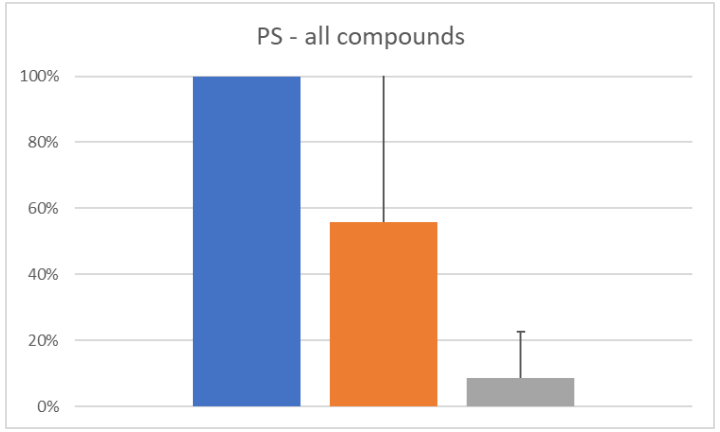
Overview of chemicals quantified in leachates from polystyrene MP

All compounds (mg/kg)



	PS		
	P	D	T
Tri-o-tolylphosphate	6.0	4.2	2.3
Tris(1-chloro-2-propyl)phosphate	3.4	1.9	0.2
Bis(2-ethylhexyl) phthalate	4.6	1.1	0.1
Dibutyl phthalate	0.1	0.1	
Alkylated benzenes (sum)	30	2.5	0.2
Benzaldehyde	3.9	2.0	
Styrene	3.6	1.0	0.7
Naphtalene	0.2		

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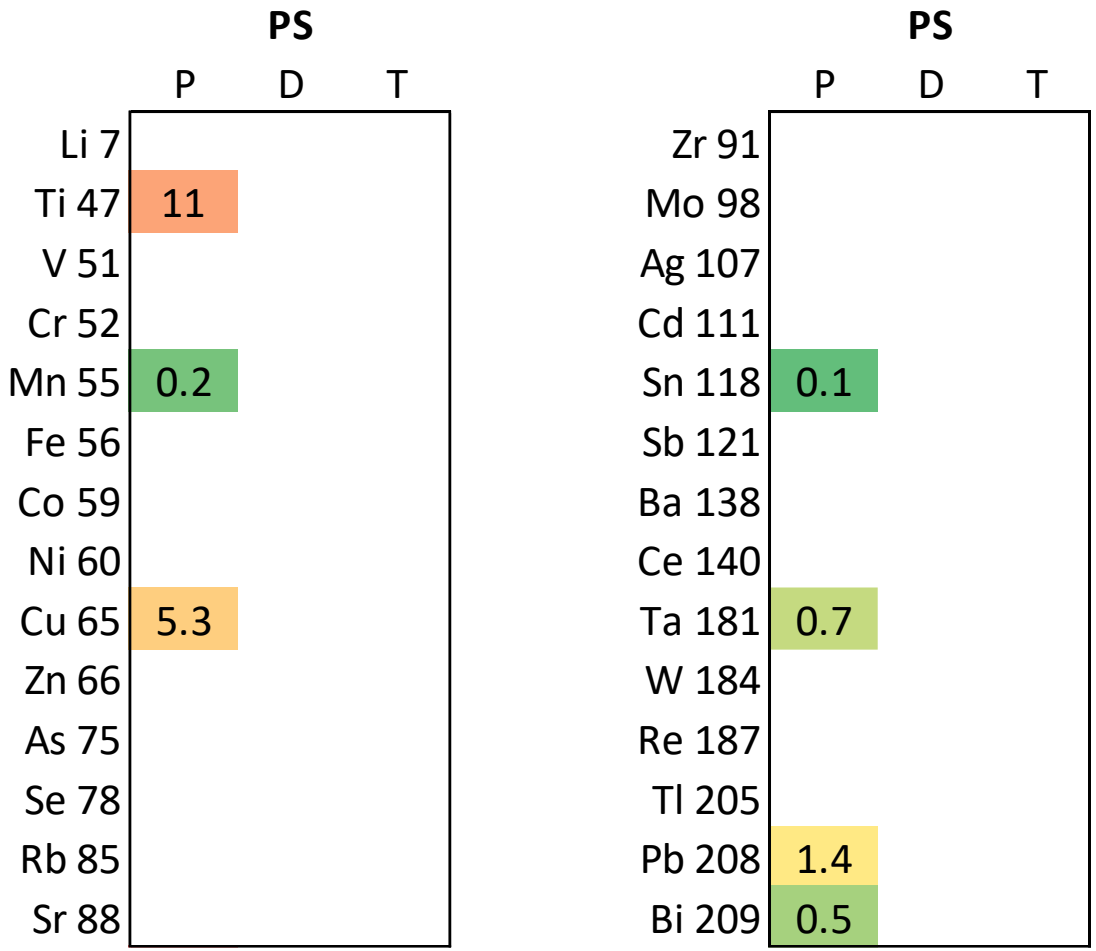
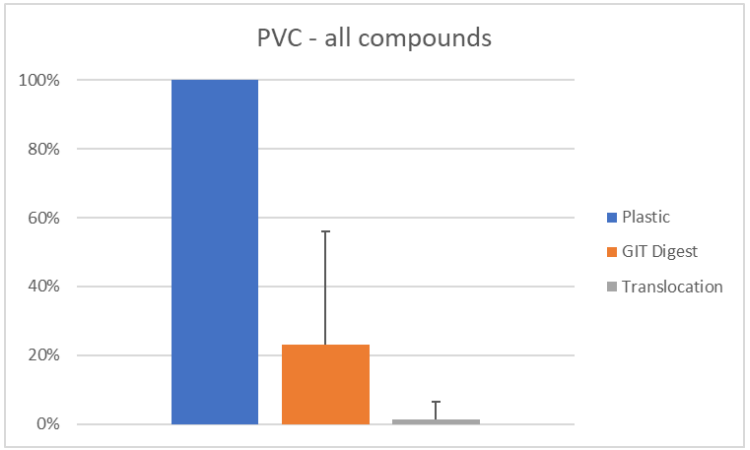
Overview of elements in plastics and leachates from polystyrene MP

Elements (mg/kg)



Overview of chemicals quantified in leachates from polyvinyl chloride MP

All compounds (mg/kg)



	PVC		
	P	D	T
Triisobutylphosphate	1.0	0.8	
Tris(1-chloro-2-propyl)phosphate	0.1		
Tris(2-chloropropyl)phosphate	0.1		
Bis(2-ethylhexyl) phthalate	4.2	2.6	0.9
Dibutyl phthalate	0.1		
Phthalic acid, di(2-propylpentyl) ester	1.2	0.6	
Phthalic acid, hept-4-yl isobutyl ester	0.1	0.1	
3,3-Dimethylheptanoic acid	1.0		
3-tert-Butyl-4-hydroxyanisole	0.9		
Benzene, 1-(chloromethyl)-2-methyl	2.2	0.1	
Benzoic acid, octyl ester	0.7		
Butanedioic acid, dimethyl ester	2.6		
Hexanedioic acid, bis(2-ethylhexyl) ester	6.7	0.2	
Hexanedioic acid, dimethyl ester	1.0		
Oxalic acid, allyl butyl ester	0.7	0.3	
Pentanedioic acid, dimethyl ester	3.0		
Naphtalene	0.5	0.4	

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Overview of elements in plastics and leachates from polyvinyl chloride MP

Elements (mg/kg)	PVC		
	P	D	T
Li 7	0.1		
Ti 47	1.4		
V 51	0.1		
Cr 52	1.4		
Mn 55	0.3		
Fe 56			
Co 59			
Ni 60			
Cu 65			
Zn 66	260		
As 75	0.1		
Se 78			
Rb 85	0.2		
Sr 88	0.8		

	PVC		
	P	D	T
Zr 91	1.5		
Mo 98	0.2		
Ag 107	1.3		
Cd 111			
Sn 118	0.1		
Sb 121			
Ba 138			
Ce 140	0.1		
Ta 181			
W 184			
Re 187			
Tl 205			
Pb 208	1.1		
Bi 209			

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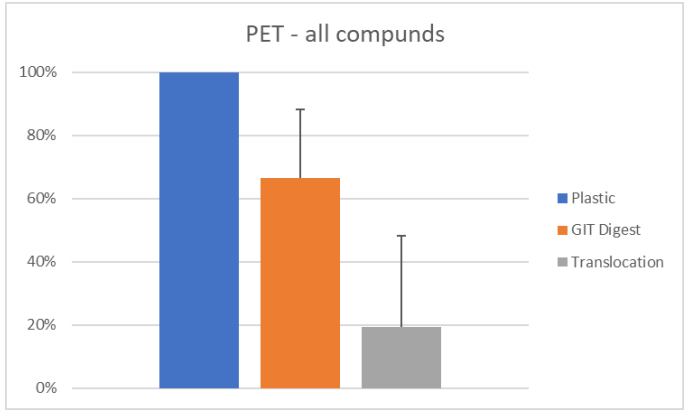
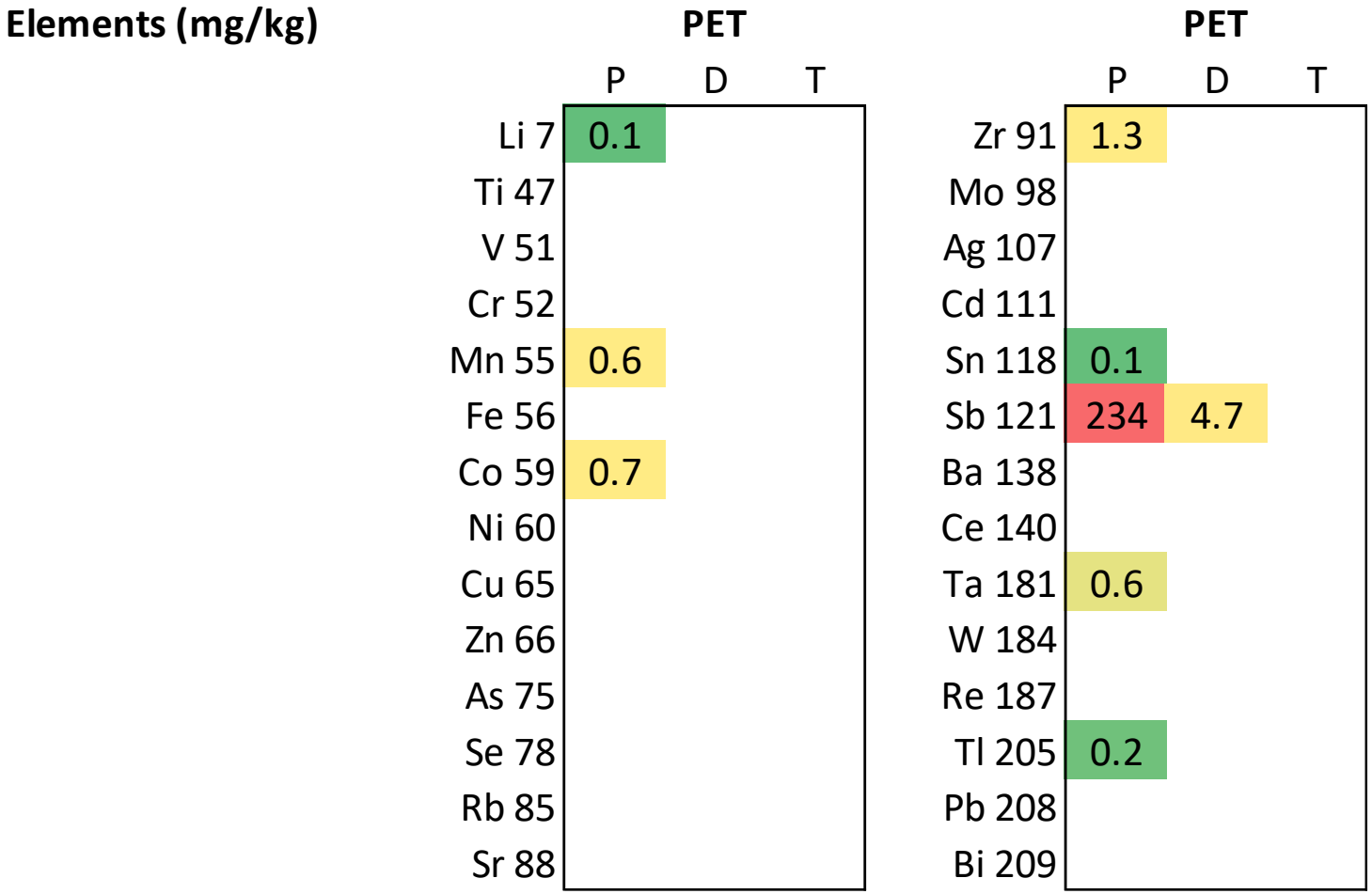
Overview of chemicals quantified in leachates from polyethylene terephthalate MP

All compounds (mg/kg)

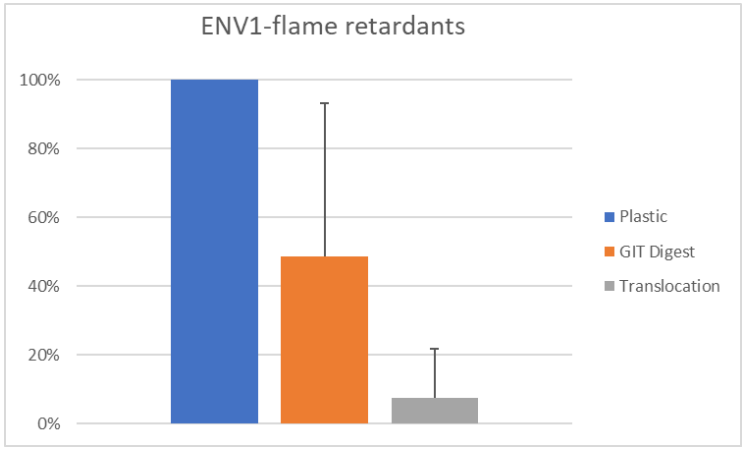
	PET		
	P	D	T
Bis(2-ethylhexyl) phthalate	1.7	0.9	0.1
Phthalic acid, di(2-propylpentyl) ester	0.4	0.2	
Tributyl acetylcitrate	0.6	0.5	0.3



Overview of elements in plastics and leachates from polyethylene terephthalate MP



Overview of flame retardants in leachates from environmental MP



Flame retardents (mg/kg)	ENV-1			ENV-3		
	P	D	T	P	D	T
Bis(1-chloro-2-propyl)-3-(3-chloropropoxy)propylphosphate	5.4	6.0		2.5	2.9	
Bis(3-chloro-1-propyl)(1-chloro-2-propyl)phosphate	4.3	5.1	0.5	2.0	1.7	1.5
Hexabromocyclododecane	1.6			2.3		
Pentabromocyclododecane	0.2			0.2		
Triethylphosphate	0.1	0.1				
Triisobutylphosphate	0.8	0.7	0.4	0.8	0.6	0.7
Tri-m-tolylphosphate	5.7	0.7				
Tri-o-tolylphosphate	6.2	0.2		3.6	0.2	
Triphenylphosphate	1.7	0.5	0.1	1.0	0.4	
Tri-p-tolylphosphate	0.9			0.8		
Tris(1-chloro-2-propyl)phosphate	7.6	4.6	0.9	5.1	1.8	0.7
Tris(2-chloroethyl)phosphate	1.6	1.4		0.7	0.7	0.1
Tris(2-chloropropyl)phosphate	1.9	1.2	0.3	3.9	0.8	0.5

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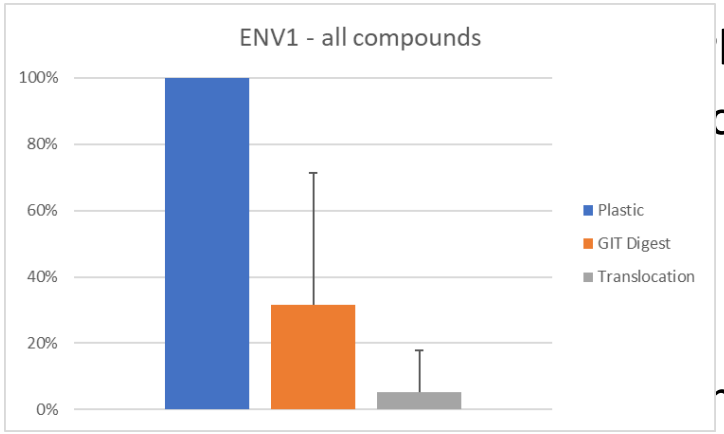
Overview of plasticizers in leachates from environmental MP



Plasticizer (mg/kg)	ENV-1			ENV-3		
	P	D	T	P	D	T
1,4-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester	3.1	2.0	0.3	1	0.7	0.2
Bis(2-ethylhexyl) phthalate	19	5.5	1.0	15	8.1	0.9
Dibutyl phthalate	2.7	0.9	0.2	0.5	0.1	0.1
Diisooctyl adipate	1.1	0.1				
Diisooctyl phthalate	7.3	5.8	1.2	5.6	3.4	1.3
hthalic acid, 2-ethylbutyl nonyl ester				5.0	3.3	1.8
c acid, 6-methylhept-2-yl nonyl ester	2.2	1.6				
Phthalic acid, di(oct-3-yl) ester				4.5	2.2	0.9
Phthalic acid, hept-3-yl nonyl ester	3.7	0.8		1.7	0.8	0.1
Phthalic acid, hex-3-yl nonyl ester	6.1	2.7	0.2	0.8	0.3	0.1
halic acid, nonyl 2-propylpentyl ester	1.6	0.1		0.4		

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Overview of environmental contaminants in leachates from environmental MP

Environmental contaminants (mg/kg)

	ENV-1			ENV-3		
	P	D	T	P	D	T
Acenaphtene	0.1			0.1		
Acenaphtylene	0.2					
Antracene	0.1					
Benz[a]anthracene	0.1			0.1		
Chrysene	0.1			0.1		
Fluoranthene	0.2			0.2		
Fluorene	0.1			0.1		
Naphtalene	0.9	0.4	0.1	0.8	0.4	0.1
Phenanthrene	0.3			0.2		
Pyrene	0.2			0.2		

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Overview of elements in plastics and leachates from environmental MP

Elements (mg/kg)	ENV-1			ENV-3		
	P	D	T	P	D	T
Li 7	1.8			1.8		
Ti 47	43			100		
V 51	3.5	0.5		3.4	0.6	
Cr 52	152	0.6		116	0.9	
Mn 55	37	5.1		29	11	
Fe 56	2099	33	14.5	1598	46	
Co 59	2.5	0.1		2.1	0.1	
Ni 60	54	1.2		33	0.9	
Cu 65	23			18		
Zn 66	172	26		109	19	
As 75	1.2			1.1		
Se 78	1.3			0.3		
Rb 85	2.0			2.1		
Sr 88	65	25	1.8	29	11	

	ENV-1			ENV-3		
	P	D	T	P	D	T
Zr 91	3.3	0.1		3.4		
Mo 98	8.6	0.5		9.0	0.5	
Ag 107	2.0			1.1		
Cd 111	17	0.5		41	0.5	
Sn 118	8.8	0.2		21	0.3	
Sb 121	4.4	0.3		4.0		
Ba 138	1544	2.6		683	2.4	
Ce 140	2.2			2.2		
Ta 181	4.0					
W 184	4.2					
Re 187	2.3					
Tl 205	4.2			0.1		
Pb 208	241	8.4		323	11.1	
Bi 209	0.2			0.3		

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Exposure to MP associated chemicals? An example with DEHP

- Estimated exposure to MP: 39,000 to 52,000 part./year (Cox et al. 2019)
- Particle size in those studies 0.1 – 1.0 mm
- Estimated exposure up to 0.14 g MP/day
- DEHP in digestion 10 mg/kg plastic, uptake 1.4 µg/day
- TDI DEHP is 0.05 mg/kg bw/day, i.e. 3.5 mg/day
- Conclusion: exposure to DEHP through microplastics is far below TDI

Exposure to MP associated chemicals? An example with caprolactam

- Estimated exposure to MP: 39,000 to 52,000 part./year (Cox et al. 2019)
- Particle size in those studies 0.1 – 1.0 mm
- Estimated exposure up to 0.14 g MP/day
- Caprolactam in digestion 50 mg/kg plastic, uptake 7 µg/day
- TDI caprolactam is 0.5 mg/kg bw/day, i.e. 35 mg/day
- Conclusion: exposure to caprolactam through microplastics is far below TDI

To summarize

- Leaching of microplastic associated chemicals into simulated digests and their translocation over an intestinal barrier in vitro was determined.

- About 50 organic chemicals were identified. While concentrations in plastic may be high, emissions into simulated digests was 0.1 to 50 mg/kg plastic. Only a few of the organic chemicals were able to translocate across the intestinal barrier in vitro.

- While many elements were found, especially in the environmental MP, only a part of these were found in the digests. Almost no elements were found to translocate across the intestinal barrier in vitro.

- Two examples show that the exposure is far below TDI for those compounds.

Thank you for your attention!

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