water

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Article

From the well to the bottle: Identifying Sources of Microplastics in Mineral Water

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Supplementary Materials

Table S1. Sampling details and microplastics (MP) findings in samples and blanks type I raw water, particle numbers rounded to integers, SD = standard deviation, LOD = limit of detection

Bottler		A	B	C	D	Mean	SD	LOD
Sample volume [L]		1014.7	1000	1212.8	1038.6			
Average flow rate sampling bypass [L/h]		150.3	2160.0	1617.1	1133.0			
Treatments applied		density separation + citric acid	-	density separation + citric acid				
Procedural Blank	total particle count	23396	23225	23792	24271	23671	403	
	non-MP	23377	23225	23773	24261	23659	401	
	MP	19	0	19	10	12	8	36
Sample	total particle count	16931	78558*	18005	63857			
	non-MP	16896	78511*	17799	63781			
	MP	35	48*	206	76			
Sample per m³	total particle count	16686	78558	14845	61484	42893	27799	
	non-MP	16651	78511	14676	61410	42812	27822	
	MP	34	48	170	73	97	53	

* = sub-sample of 20% examined and extrapolated.

Table S2. Sampling details and microplastics (MP) findings in samples and blanks type II de-ferrized water, particle numbers rounded to integers, SD = standard deviation, LOD = limit of detection.

Bottler		A	B	C	D	Mean	SD	LOD
Sample volume [L]		1001.2	1000	1025.3	1453.2			
Average flow rate sampling bypass [L/h]		129.2	2160.0	1235.3	1089.9			
Treatments applied		citric acid	-	citric acid	citric acid			
Procedural Blank	total particle count	24318	23225	23168	24663	23844	659	
	non-MP	24309	23225	23159	24663	23839	659	
	MP	10	0	10	0	5	5	20
Sample	total particle count	37507	19221	34324	21583			
	non-MP	37488	19202	34270	21517			
	MP	19	19	54	67			
Sample per m³	total particle count	37462	19221	33477	14852	26253	9451	
	non-MP	37443	19202	33425	14807	26219	9452	
	MP	19	19	53	46	49	3	

Table S3. Sampling details and microplastics (MP) findings in samples and blanks type IIIa cleaned glass bottles, particle numbers rounded to integers, SD = standard deviation, LOD = limit of detection.

Bottler		A	B	C	D	Mean	SD	LOD
Fresh water rinsing per bottle [mL]		235	1000	140	210			
Bottle volume [L]		0.75	0.75	0.75	0.70			
Number of bottles examined		3	3	3	3			
Procedural blank	total particle count	887	1945	1036	469	1084	539	
	non-MP	880	1932	1029	440	1070	542	
	MP	6	13	6	29	13	9	40
Sample	total particle count	13270	295	260	1371			
	non-MP	13216	269	241	1362			
	MP	54	25	19	10			
Sample per L	total particle count	5898	131	115	653	1699	2434	
	non-MP	5874	120	107	648	1687	2427	
	MP	24	11	8	5	12	7	

Table S4. Sampling details and microplastics (MP) findings in samples and blanks types IIIb Filled and V filled and capped glass bottles, particle numbers rounded to integers, SD = standard deviation, LOD = limit of detection.

Bottler		A (V)	B (V)	B (IIIb)	C (V)	D (V)	Mean	SD	LOD
Carbonization		no	no	no	no	no			
Bottle volume [L]		0.75	0.75	0.75	0.75	0.70			
Number of bottles examined		3	3	3	3	3			
Procedural blank	total particle count	887	1945		1036	469	1084	539	
	non-MP	880	1932		1029	440	1070	542	
	MP	6	13		6	29	13	9	40
Sample	total particle count	1921	1143	225	2568	453			
	non-MP	1751	238	212	994	263			
	MP	169	906	13	1574	190			
Sample per L	total particle count	854	508	100	1142	216	680*	349*	
	non-MP	778	106	94	442	125	363*	275*	
	MP	75	403	6	700	90	317*	257*	

* = calculated only from sample type (V)

Table S5. Sampling details and microplastics (MP) findings in samples and blanks types IVa and IVb Particles in caustic cleaning solutions, SD = standard deviation, LOD = limit of detection, means and SD calculated only from samples marked with *.

Bottler		A*	D*	B*	C*	D, Plus 6 Months	D After Renewal	D NaOH-Detergent Concentrate	Mean	SD	LOD
Caustic treatment		sedimentation, lastly June 21st 2019	sedimentation every 12 weeks, lastly about 6 weeks ago	bypass filtration	none	sedimentation every 12 weeks,	n/a	n/a			
Sample volume [mL]		885	1068	1059	870	1125	850	214			
Sub-sample examined		30%	100%	100%	32%	50%	50%	73%			
Treatments applied		Fenton, Ascorbic acid, Cellulase, Fenton, Ascorbic acid						sieving			
Procedural blank	MP	38		16			53		27*	11*	81*
Sample	MP	852	523	2942	225	2109	1798	2036			
Sample per L	MP	3240	489	2778	797	3750	4230	13079	1826*	1199*	

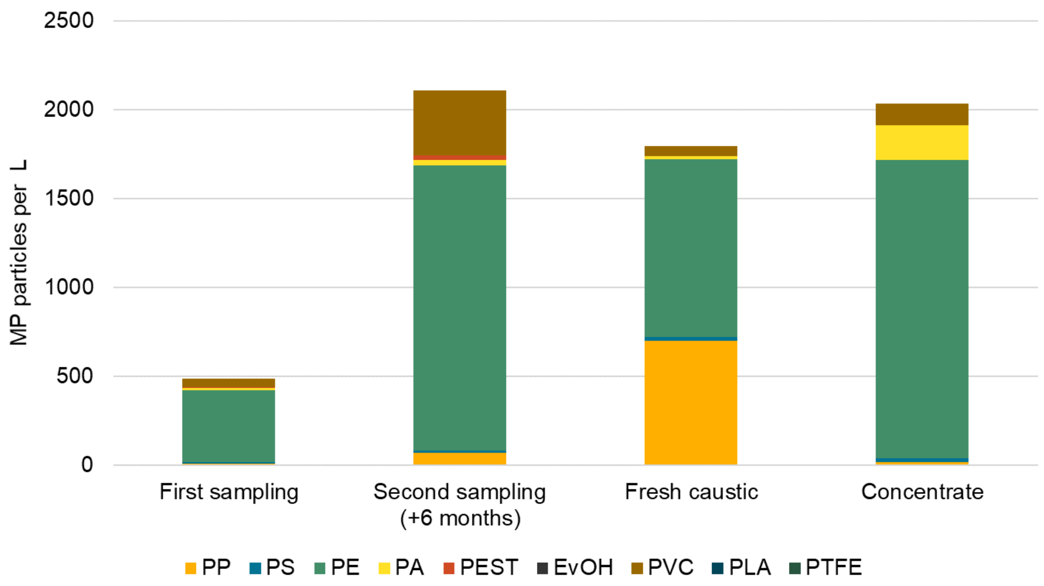


Figure S1 MP concentrations in caustic cleaning solution from bottler D in first and second sampling, fresh caustic and caustic concentrate.

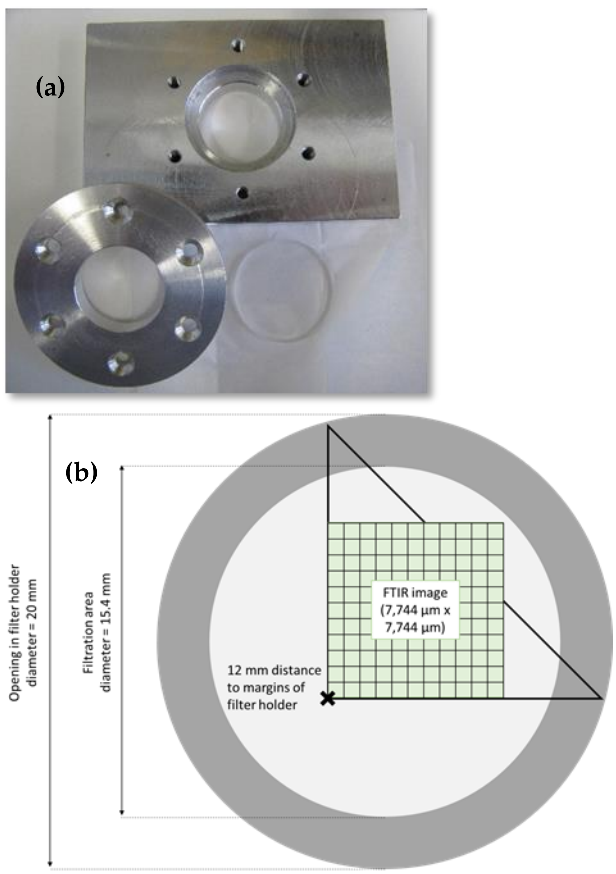


Figure S2. Holder for Anodisc filters (**a**) and measured area (**b**).

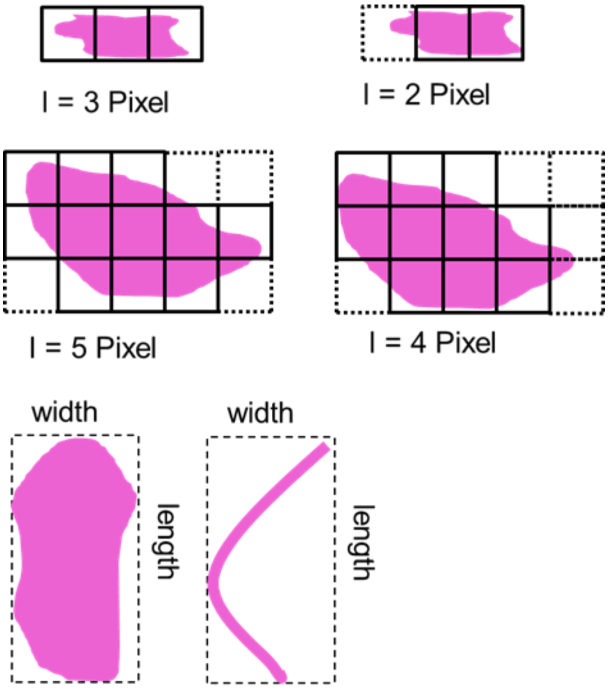


Figure S3. Particle size determination in FTIR images. Pixel grid laid over particle inevitably leads to fuzziness in particle size determination through IR images of at least +/− 1 pixel.

Feret diameters visualized. Threshold for fiber identification (length ≥ 3 x width) may sometimes mistake fibers for fragments.

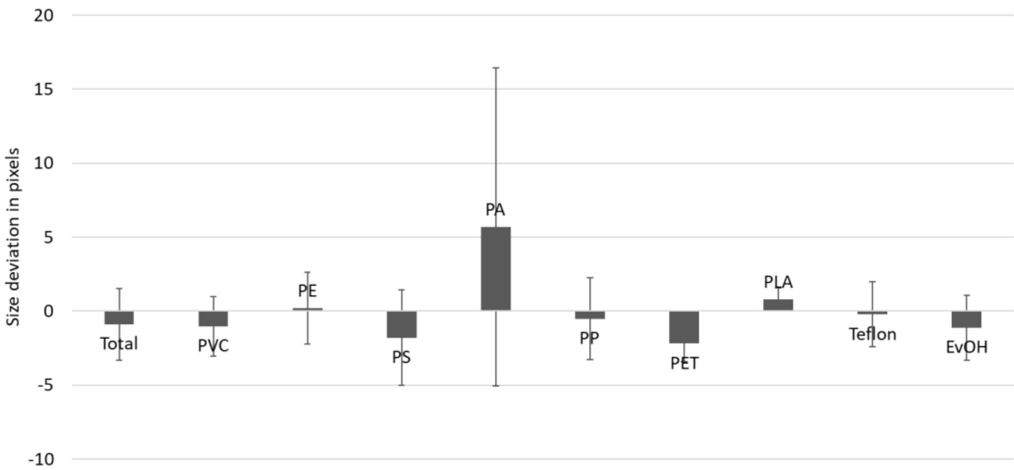
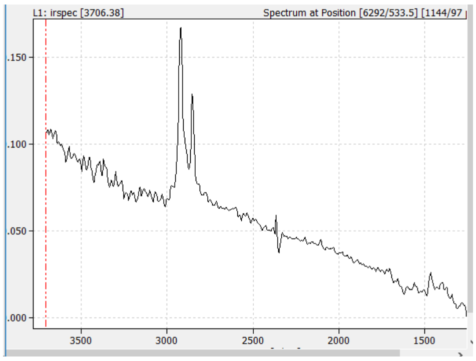
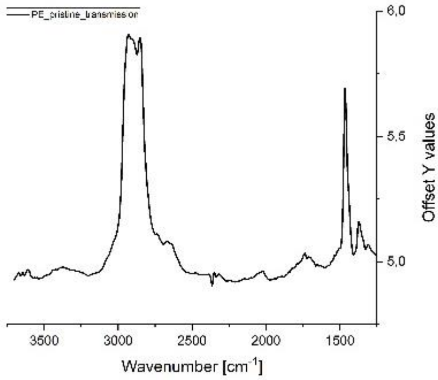
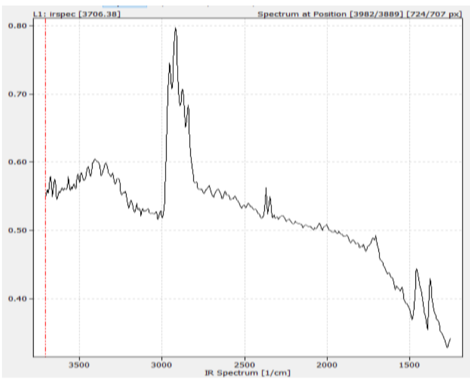
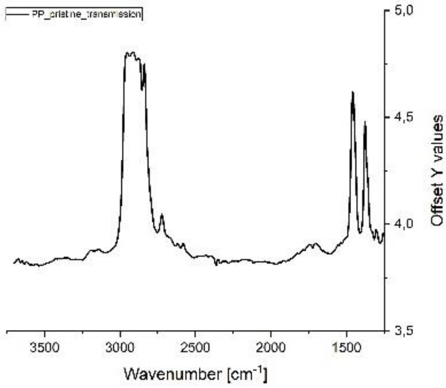
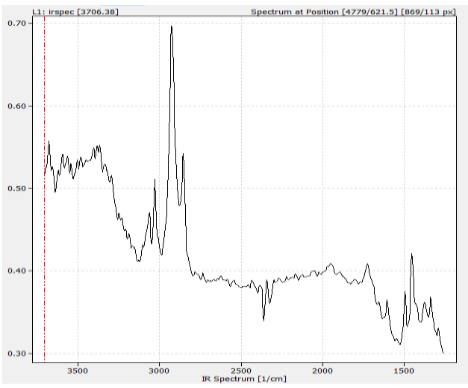
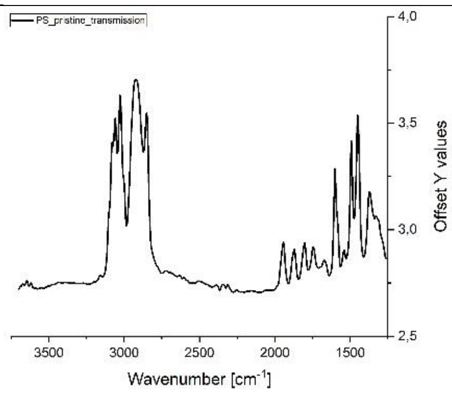
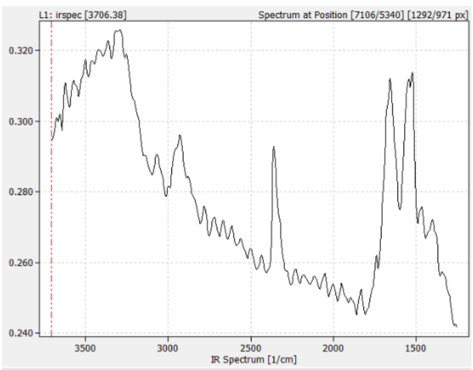
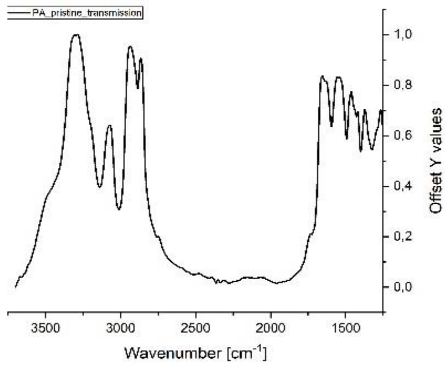
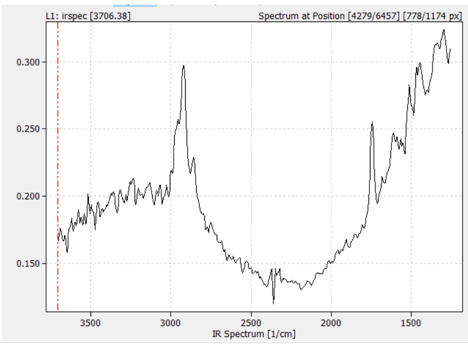
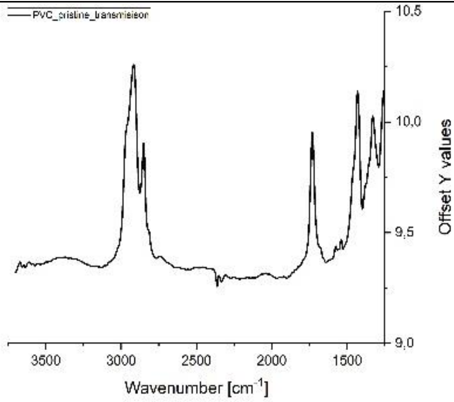
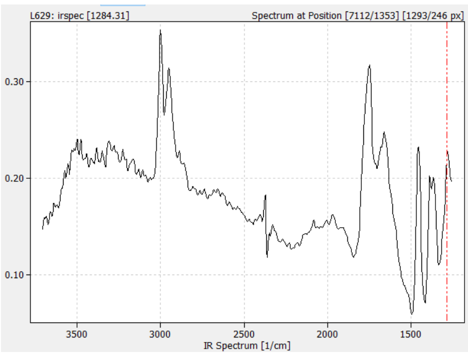
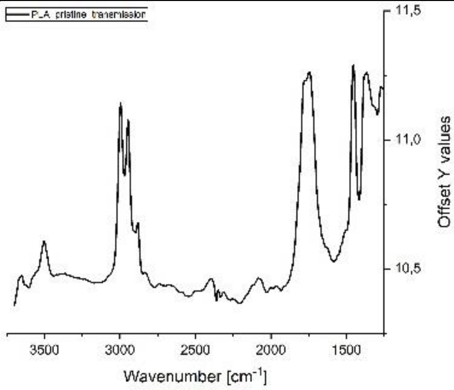
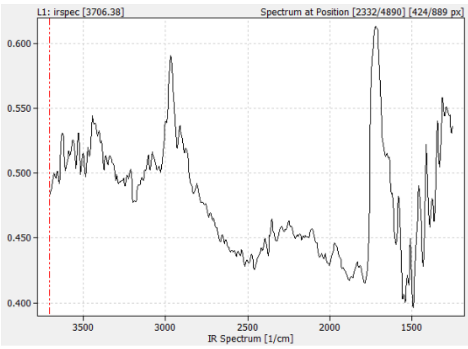
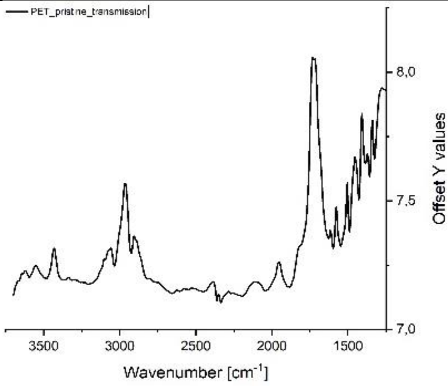
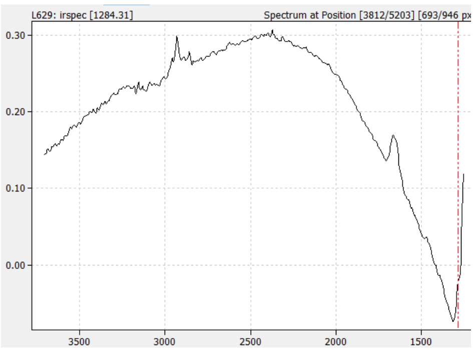
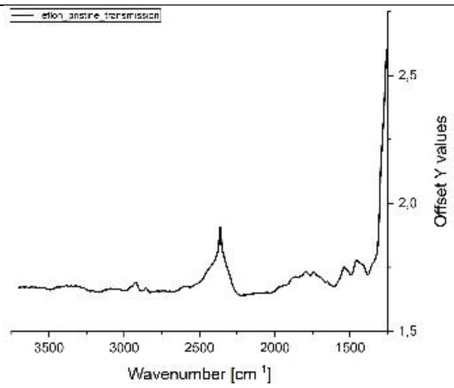
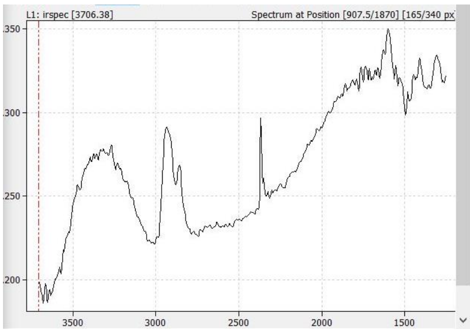
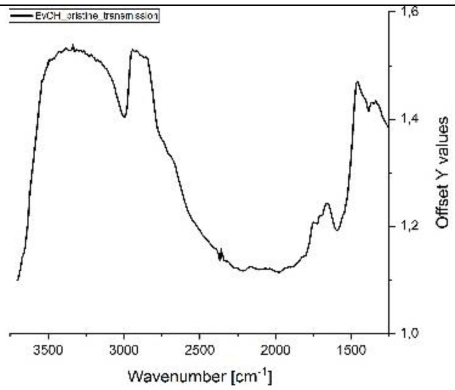


Figure S4. Deviation of particle dimensions determined in photo (reference) and IR images (n = 122). Bars show standard error.

Table S6. Example spectra of smallest particles detected. Note that compared to the reference particles, spectra of the smallest particles detected tend to strong baseline drifting and distortion effects.

Polymer	Particle Major and Minor Dimensions, Derived from IR Image [µm]	IR Spectrum of smallest particle detected	IR spectrum of reference particle (~ 100 µm)
PE	11.0 x 5.0		
PP	11.0 x 5.0		
PS	11.0 x 5.0		
PA	11.0 x 5.0		

Polymer	Particle Major and Minor Dimensions, Derived from IR Image [µm]	IR Spectrum of smallest particle detected	IR spectrum of reference particle (~ 100 µm)
PVC	11.0 x 11.0		
PLA	16.5 x 16.5		
PET	11.0 x 11.0		
PTFE	21.06 x 17.17		

Polymer	Particle Major and Minor Dimensions, Derived from IR Image [µm]	IR Spectrum of smallest particle detected	IR spectrum of reference particle (~ 100 µm)
EvOH	11.0 x 11.0		

Note on detection of PTFE particles on Anodisc filters:

Hemp was chosen for sealing pipefittings as an alternative to PTFE tape, which is very commonly used. PTFE was indeed found in two of the raw water samples and it is very likely that more PTFE particles were overlooked: it is hardly detectable on Anodisc filters because its characteristic absorption bands lie at the margin of their IR-transparency limit at 1250 cm^{-1}. Measurements on reference PTFE particles, however, showed that they can still be detected under ideal conditions. Therefore, as a proof of principle, it was attempted to detect PTFE under real conditions, which was possible in some cases. However, regarding the high potential of sample contamination by hemp fibers, we would recommend to rather use PTFE or some other polymeric tape for sealing when PTFE is not among the target polymer classes. If one chose to use other filter substrates like silicon, which opens the spectral range below 1300 cm−1 [1] and targets PTFE particles in the analysis, PTFE tape of course cannot be used. Then hemp might still be an alternative, when care is taken to keep it from entering the sample.

Table S7. Confusion matrix for evaluation of Random Decision Forest Model for all classes. Grey indicates true positives.

	Anodisc	Filter Holder	PP	PS	PE	PA	PET	EvOH	PVC	PLA	Teflon	Cellulose	Skin/Hair	Anodisc_Impurity_Type_1	Anodisc_Impurity_Type_2	Anodisc_Impurity_Type_3	Anodisc_Impurity_Type_4
Anodisc	401	0	7	0	0	0	0	0	1	0	1	0	0	0	0	0	0
Filter holder	0	390	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PP	16	0	363	1	20	0	0	0	4	0	1	0	0	2	2	0	1
PS	3	0	1	401	1	0	0	0	0	0	2	0	0	1	1	0	0
PE	0	0	3	0	391	0	0	0	0	0	0	0	0	10	4	0	2
PA	0	0	0	1	0	406	0	0	0	0	0	1	2	0	0	0	0
PET	0	0	1	3	0	0	398	0	6	0	1	0	0	0	1	0	0
EvOH	0	0	0	0	0	0	0	399	0	0	0	0	1	0	0	0	0
PVC	0	0	3	2	1	0	1	0	382	5	6	0	0	0	0	0	0
PLA	2	0	0	0	0	0	2	0	0	406	0	0	0	0	0	0	0
Teflon	3	0	0	0	3	0	0	0	4	0	375	1	2	1	1	0	0
Cellulose	0	0	2	0	0	0	0	1	0	0	2	374	12	2	1	14	2
Skin/Hair	0	1	1	0	0	1	0	0	0	0	1	6	384	1	1	4	0
Anodisc_impurity_type_1	0	0	3	1	2	0	0	0	0	0	3	0	1	228	9	0	3
Anodisc_impurity_type_2	0	0	0	0	2	0	0	1	0	0	0	5	4	9	166	1	2
Anodisc_impurity_type_3	0	0	1	0	0	1	0	1	0	0	1	9	7	4	3	233	0
Anodisc_impurity_type_4	0	0	1	0	0	0	0	0	0	0	0	0	0	3	7	1	68

$$Accuracy = \frac{TP+TN}{TP+TN+FP+FN} \in [0,1], \text{ calculated over all classes} \quad (1)$$

$$Sensitivity = \frac{TP}{TP+FN} \in [0,1], \text{ calculated for each class} \quad (2)$$

$$Precision = \frac{TP}{TP+FP} \in [0,1], \text{ calculated for each class} \quad (3)$$

$$Specificity = \frac{TN}{TN+FP} \in [0,1], \text{ calculated for each class} \quad (4)$$

TP = true positive, TN = true negative, FP = false positive, FN = false negative.

Table S8. Evaluation results for Random Decision Forest Model.

	Sensitivity	Precision	Specificity
Anodisc	0.9780	0.9957	0.9435
Filter holder	1.0000	0.9998	0.9974
PP	0.8854	0.9959	0.9404
PS	0.9780	0.9986	0.9804
PE	0.9537	0.9948	0.9310
PA	0.9902	0.9996	0.9951
PET	0.9707	0.9995	0.9925
EvOH	0.9975	0.9995	0.9925
PVC	0.9550	0.9973	0.9622
PLA	0.9902	0.9991	0.9878
Teflon	0.9615	0.9968	0.9542
Cellulose	0.9122	0.9961	0.9444
Skin/Hair	0.9600	0.9949	0.9298
Anodisc_impurity_type_1	0.9120	0.9943	0.8736
Anodisc_impurity_type_2	0.8737	0.9949	0.8469
Anodisc_impurity_type_3	0.8962	0.9965	0.9209
Anodisc_impurity_type_4	0.8500	0.9983	0.8718

Table S9. Considerations for comparison with other studies.

Sample type	Study	Detection Method and Limit	Total MP Mean	Total MP SD	MP > 10 μm [%]	MP > 10 μm Mean	MP > 10 μm SD
Ground water	[2]	FTIR > 20 μm	3.7 MP m^{-3}	2.5 MP m^{-3}	100	3.7 MP m^{-3}	2.5 MP m^{-3}
	Derived from Figure 3						
Treated drinking water from ground water sources	[2]	FTIR > 20 μm	0.91 MP m^{-3}	0.80 MP m^{-3}	100	0.91 MP m^{-3}	0.80 MP m^{-3}
	Derived from Figure 3						
	[3]	Raman > 10 μm	0 MP m^{-3}	0 MP m^{-3}	n/a	n/a	n/a
	[4]	FTIR > 6.6 μm	174 MP m^{-3}	405 MP m^{-3}	98	171 MP m^{-3}	398 MP m^{-3}
	Derived from reported total particle numbers (only FTIR results) and particle size distribution in Figure 4b						
Still mineral water in glass bottles	[5]	Raman > 1,5 μm	3074 MP L^{-1}	2531 MP L^{-1}	6.9	212 MP L^{-1}	175 MP L^{-1}
	Derived from reported total particle numbers and particle size distribution in Figure 3						
	[6]	Raman > 5 μm	50 MP L^{-1}	52 MP L^{-1}	56	28 MP L^{-1}	29 MP L^{-1}
	Derived from reported total particle numbers and particle size distribution in Figure						
Cleaned glass bottles	[7]	Raman > 1,5 μm	7443 MP L^{-1}	3919 MP L^{-1}	7	487 MP L^{-1}	257 MP L^{-1}
	Derived from reported total particle numbers and mean particle size distribution in Figure 5.2, excluding results for Brand 1-2 (after caustic renewal)						

Restricted to peer-reviewed studies applying spectroscopic methods on similar types of samples, i.e. no mineral water in PET bottles or drinking water from surface waters. Where the detection limit was < 10 μm, the number of MP > 10 μm was calculated from total MP numbers and particle size distribution. Both were given in most cases. If not so, they were estimated from figures in the publications.

References

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