Entry of Microplastics into Packaged Food and Beverages – the Example of Bottled Mineral Water

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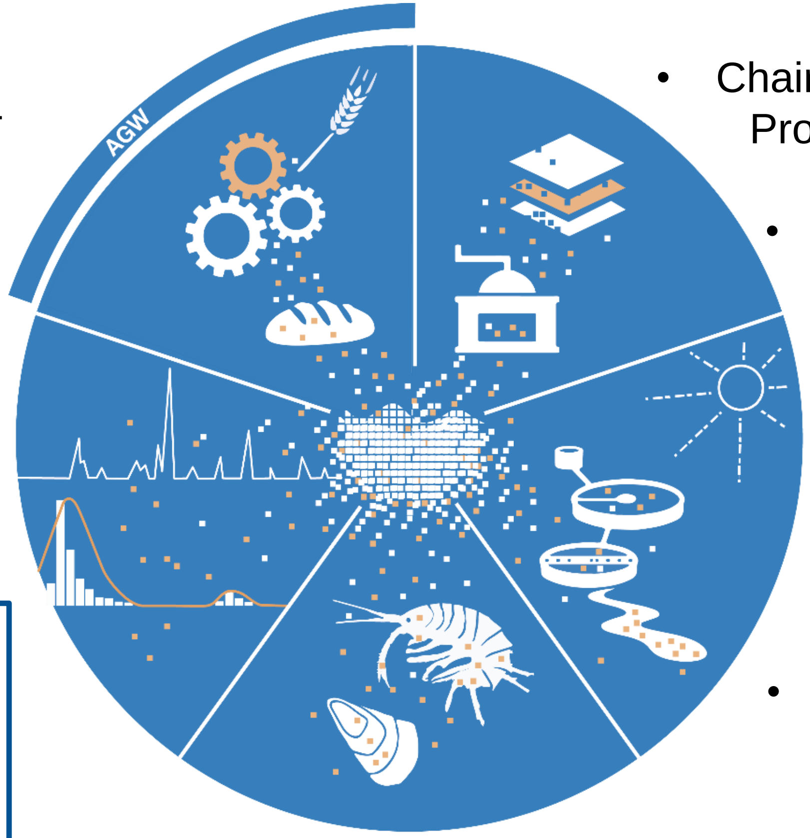
The project MiPAq: Microplastics in the Aquatic Environment and in Foodstuffs

Group of Water Systems Egineering (Dr. Karl Glas)

→ Focus on Microplastics in food and beverages



- Chair of Brewing and Beverage Technology, Prof. Thomas Becker
- Chair of Urban Water Systems Engineering, Prof. Jörg Drewes
- Chair of Aquatic Systems Biology, Prof. Jürgen Geist
- Institute of Hydrochemistry, Prof. Elsner, PD Ivleva
- 15 companies: food producers, packaging manufacturers, water treatment, analytics

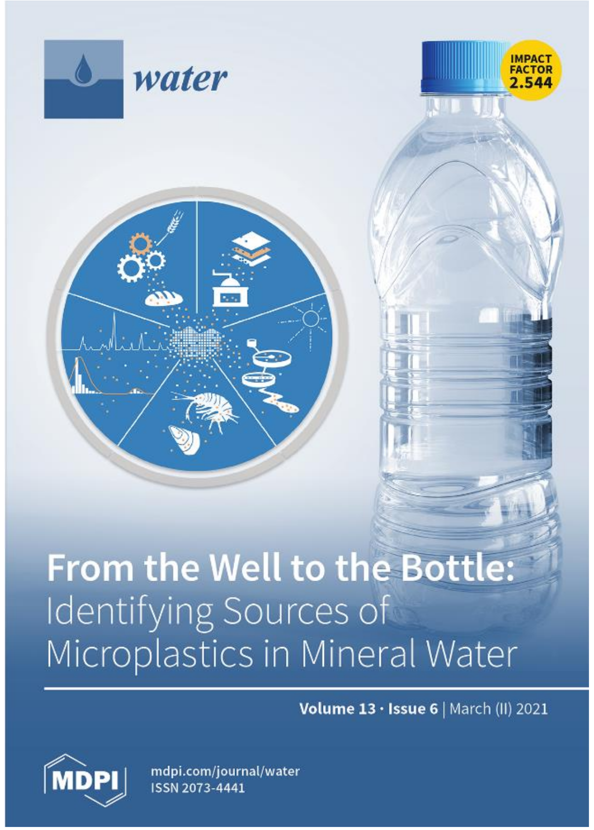
Website:
www.wasser.tum.de/en/mipaq/home/

Funded by:

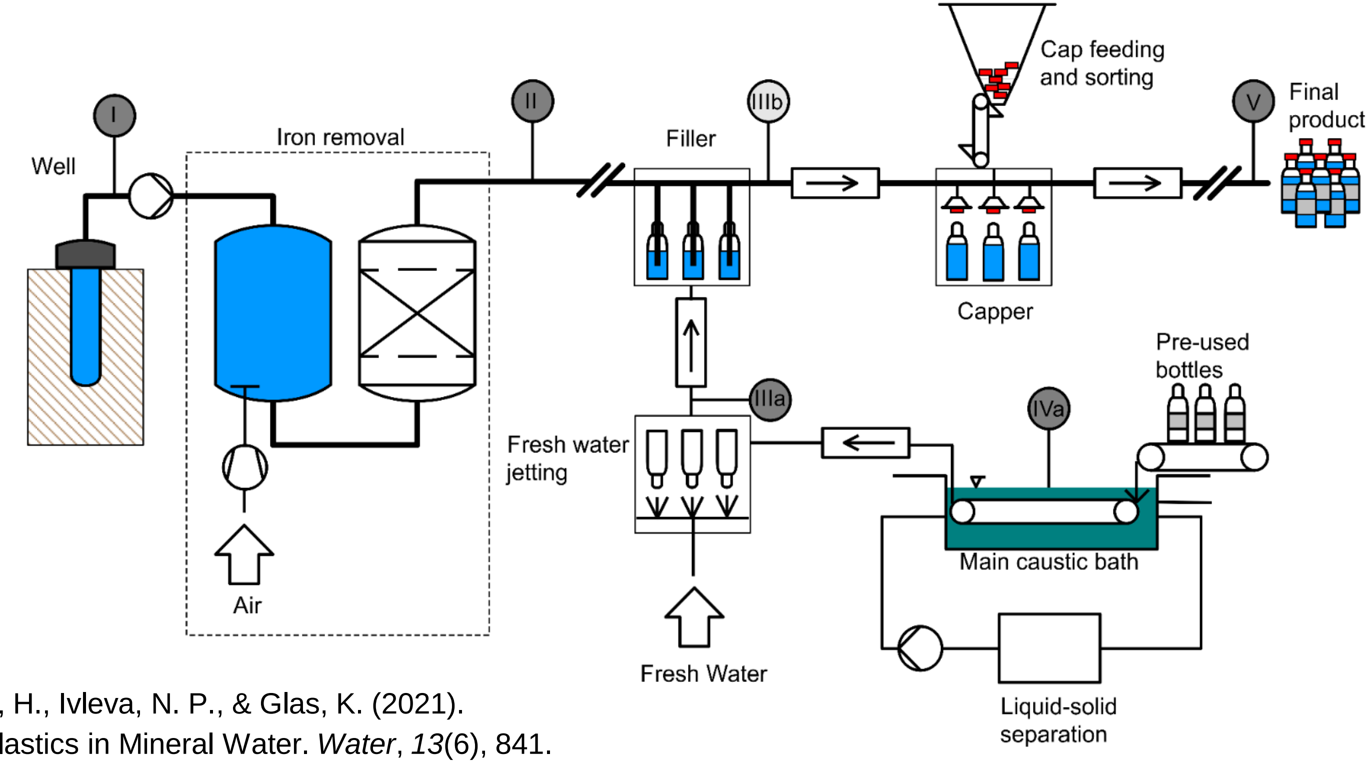
Bayerische Forschungsstiftung

Figure: Theresa Finkel

A holistic approach for the identification of MP entry paths



- Identifcation of MP sources is a prerequisite for mitigation
- Presumption: MP entry into re-usable bottles via bottle cleaning process
- Focus on still mineral water in re-usable glass bottles
- Involvement of four project partners: access to bottling and bottle cleaning process



Weisser, J., Beer, I., Hufnagl, B., Hofmann, T., Lohninger, H., Ivleva, N. P., & Glas, K. (2021). From the Well to the Bottle: Identifying Sources of Microplastics in Mineral Water. *Water*, *13*(6), 841.

Sampling and sample preparation

Sample volume	≥ 1000 L		3 bottles à 0.7 or 0.75 L		1 L
	Raw water (I)	Deferrized water (II)	Cleaned bottles (IIIa)	Filled bottles (IIIb, V)	Caustic (IVa)
	Pressurized air	Pressurized air	Surface rinsing	Surface rinsing	Filtration
	Filtration	Filtration	2 x flush with SDS 0,2%	Water on Anodisc	Fenton+Ascorbic Acid (3 h)
	Density separation (24 h)	Citric acid (24 h)	1 x flush with EtOH (30%)	2 x flush with SDS 0,2%	Filtration
	Filtration	Filtration	Anodisc	1 x flush with EtOH (30%)	Cellulase (24 h)
	Citric acid (24 h)	Anodisc		Anodisc	Filtration
	Filtration				Fenton+Ascorbic Acid (3 h)
	Anodisc				Filtration
					Anodisc

Stainless steel cartridge filters,
5 and 50 µm

Sample Process blank

Procedures according to [1, 2, 3]

In-use caustic cleaning solution

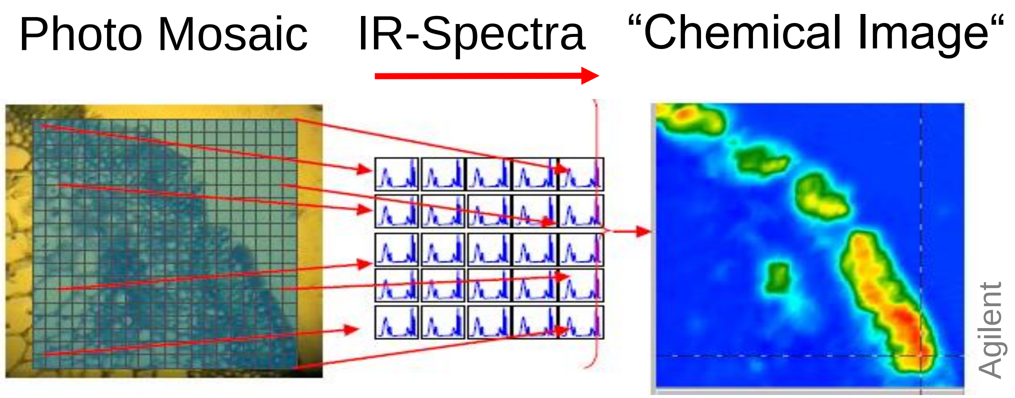
Data acquisition and analysis

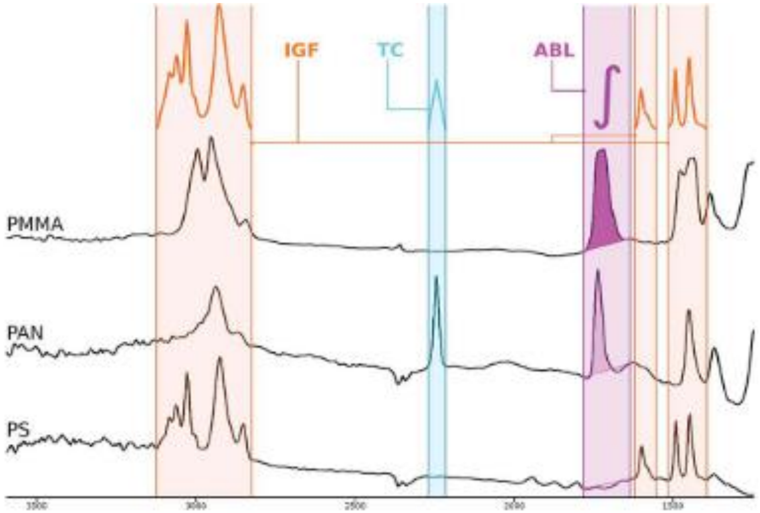
FTIR Imaging System Agilent Cary 620/670

- 128 x 128 pixels FPA detector
- 15x objective → 5.5 µm/pixel
- Lower particle size 11 µm
- 32% of each sample filter (≈ 60 mm²)
- ~ 2 mio. spectra

Random Decision Forest Model in EPINA ImageLab

- Test/Training data set of ~ 6000 spectra
- Includes: PE, PP, PET, PS, PVC, PA, PTFE, PLA, EvOH, cellulose, proteins
- Monte-Carlo cross validation
- Model accuracy 95.45%

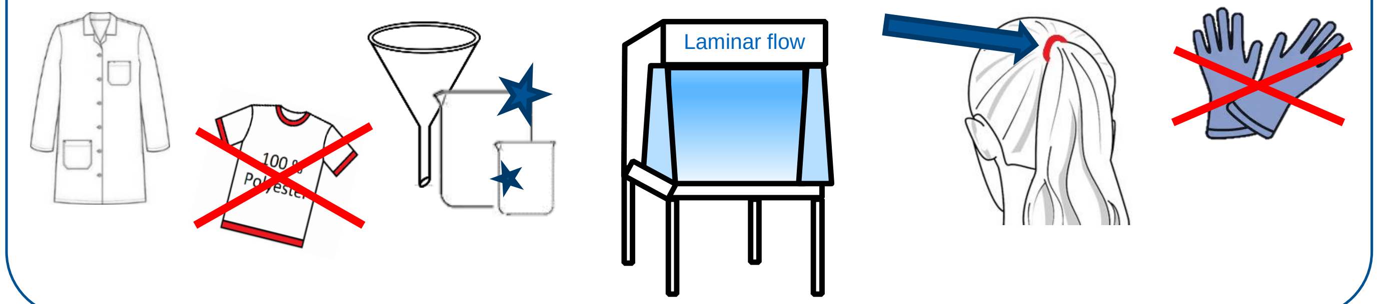




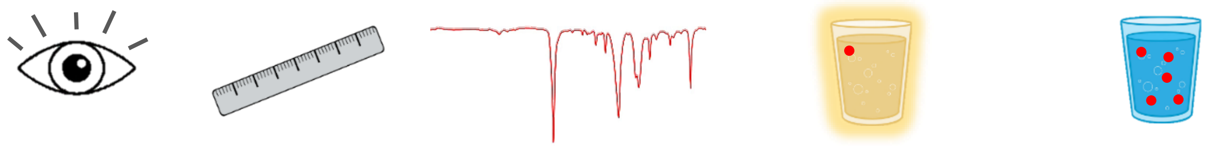
[5]

Quality Assurance and Quality Control

General Precautions

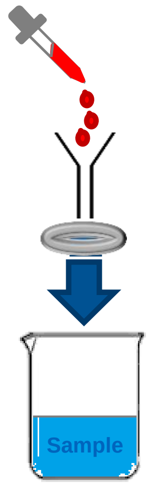


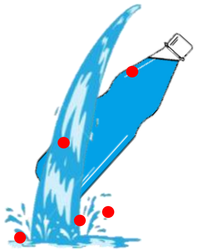
Quality assurance – Validation



Control entire process | Size calibration | Polymer identification | LOD = blank ± 3*SD | Recovery rates

Specific Precautions





Rinse sampling container before entering clean area

Check used chemicals for contamination

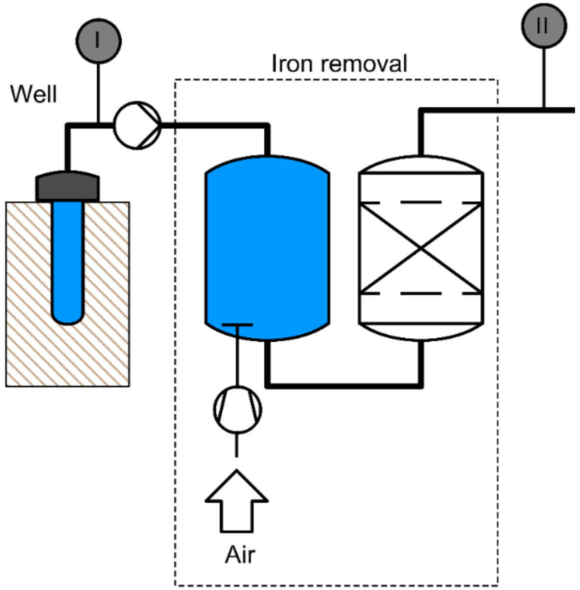
Sampling

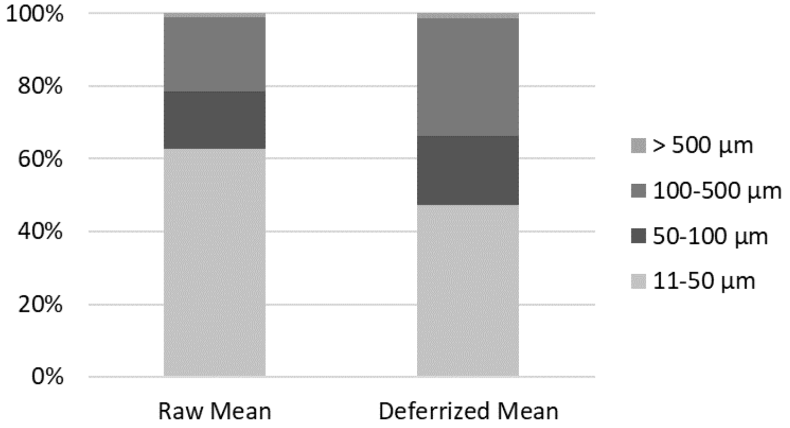
1x ✓
3x ✓✓

One bottle or 100s to 1000s of liters

Pictures (partly modified) from this colloquium's e-poster and submitted paper
Schymanski D. & Oßmann B. E. et al., *„Analysis of Microplastics in Clean Water: Minimum Requirements and Best Practice Guidelines"*

Results MP in mineral water from the well…

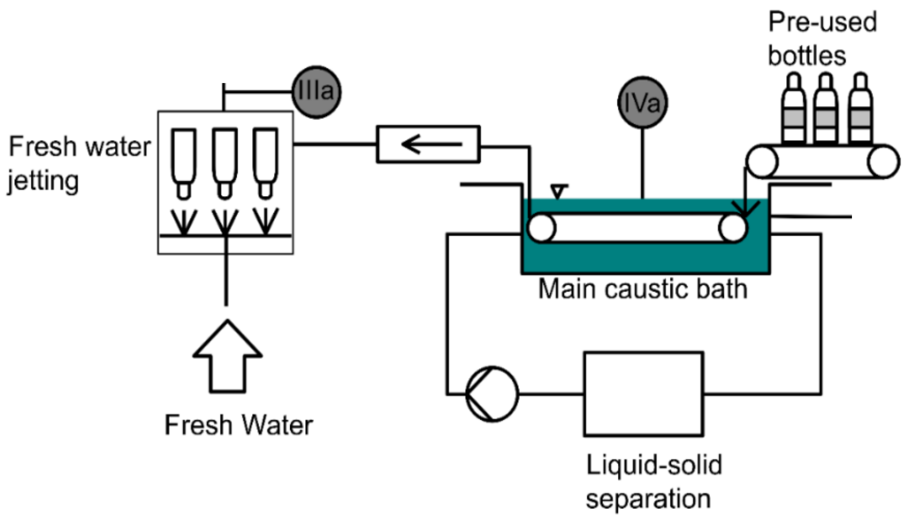


Sample type	Raw Water (I)	Deferrized Water (II)
LOD	36	20
MP concentration ≥ 11 µm	48-170 MP m^{-3}	< LOD - 53 MP m^{-3}
Most abundant polymers	46% PVC, 34% polyesters	35% PVC, 29% PA, 26% polyesters
Particle sizes [µm], larger Feret diameter		
Particle shapes	Fragments 89-100% Fibers 0-11 %	Fragments 83-95% Fibers 5-17 %

→ Mineral water << 1 MP L^{-1}

→ In accordance with other studies using spectroscopic methods[1, 6]

…across the bottle washing process…



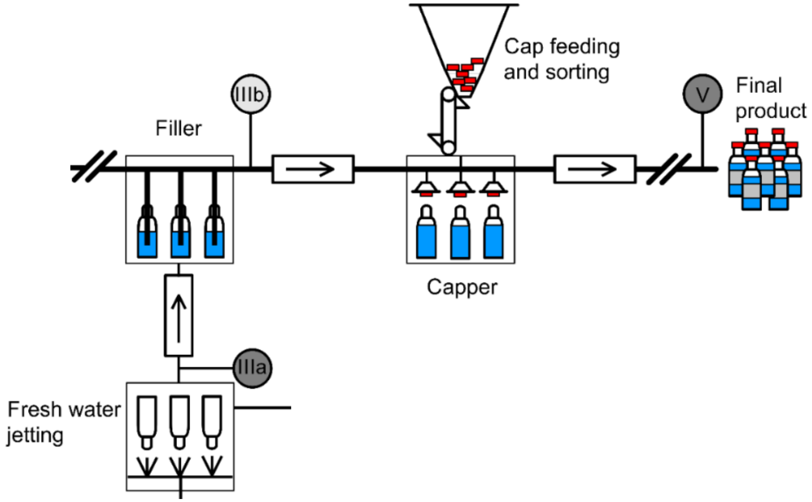
Sample type	Caustic (IVa)	Cleaned Bottles (IIIa)
LOD	81	40
MP concentration ≥ 11 µm	489-3,240 MP L^{-1}	< LOD
Most abundant polymers	Three samles: 67-81% PE, One sample: 62% PP	n/a

→ No carryover of MP from caustics to bottles for particle types and sizes investigated

→ Fresh water jetting seems successful

→ Carryover for non-IR active substances and particles < 11 µm cannot be ruled out[7]

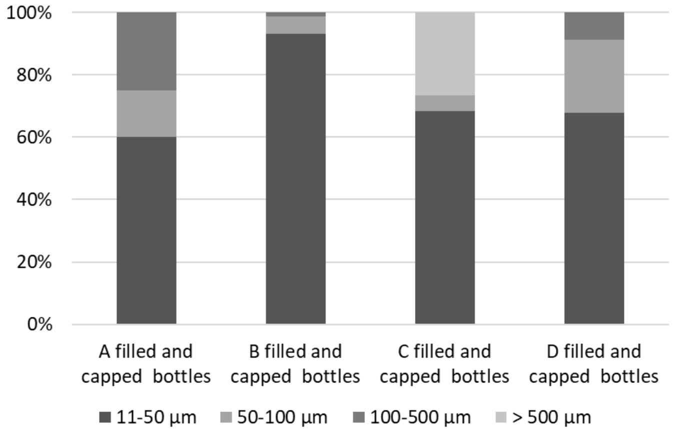
…to filled and capped bottles



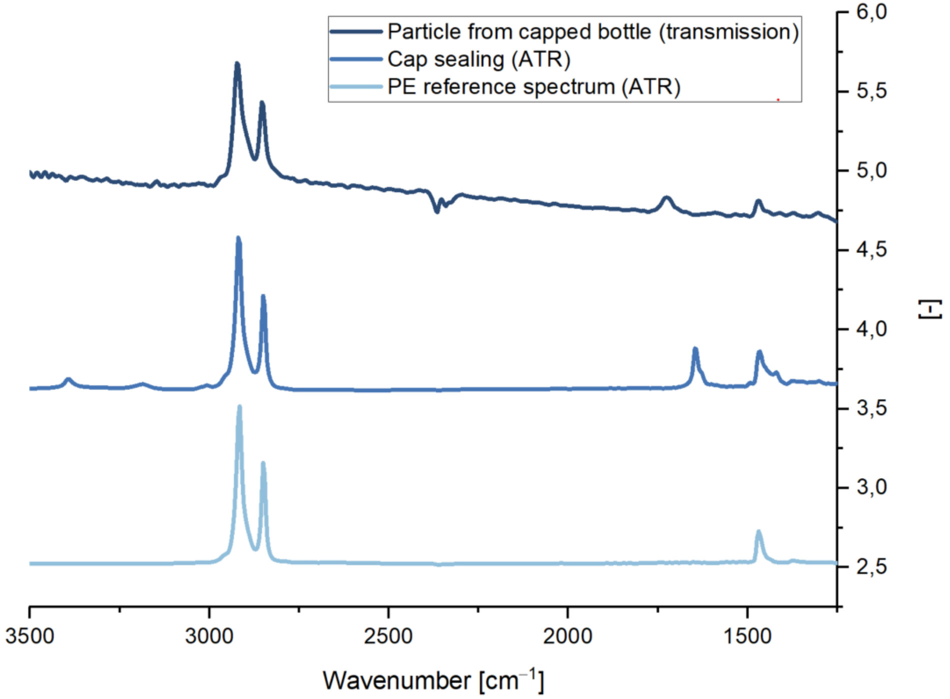
→ Sharp rise of MP concentrations after bottle capping

→ Concentrations and polymer species in accordance to literature[8,9]

→ High abundance of PE particles

Sample type	Cleaned Bottles	Filled Bottles	Filled & Capped Bottles
LOD	40	40	40
MP concentration ≥ 11 µm	< LOD	< LOD	75-700 MP L^{-1}
Most abundant polymers	n/a	n/a	81% PE 11% PS
Particle sizes [µm], larger Feret diameter	n/a	n/a	
Particle shapes	n/a	n/a	Fragments 76-98% Fibers 2-24%

Abrasion from cap sealings identified as the main entry path



Repeated opening and closing of PET bottles with HDPE cap is known to produce MP[10,11]

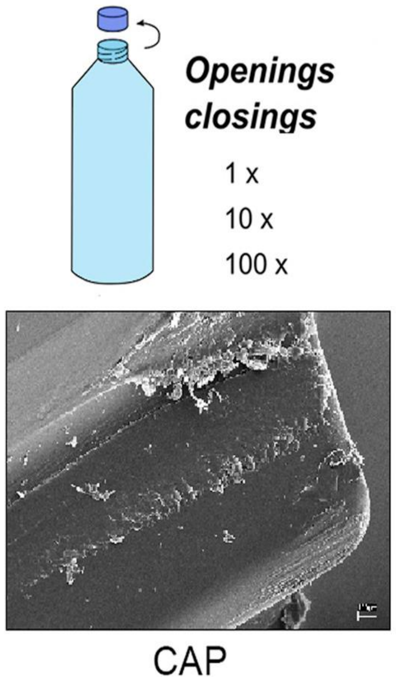


Figure modified from [10]

→ Bottle cap sealings show very similar spectra to PE

→ Product data sheet: „PVC-free soft polyolefin“, various qualities available

→ Remarkable: samples with the highest MP concentrations had caps with the same sealing variant

Results wrap-up from this and other studies

Entry paths for MP in mineral water	
Bottle material and type	++ [8,9]
Cap abrasion	++ [10]
Carbonization	+ [8]
Bottle age	+ [9]
Filling process	−
Bottle cleaning residues	+ (particles < 11 µm) [7] − (particles ≥ 11 µm)

++ empirical correlation
+ Correlation suspected
- No correlation

Main findings:

→ Caustic did not leave particles (≥ 11 µm) in bottles
→ Very low (< 1 MP L^{-1}) concentrations in mineral water itself
→ Abrasion from cap sealings is the main entry path for MP ≥ 11 µm

Implications for science and food industry

→ Test different cap (sealing) materials
→ Test suction or rinsing of caps
→ Keep bottle washer caustics clean
→ Do not further reduce fresh water jetting
→ Collaborate to find suitable and doable solutions

References

Photos and Illustrations by Jana Weisser unless otherwise stated

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Thank you for your attention!

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