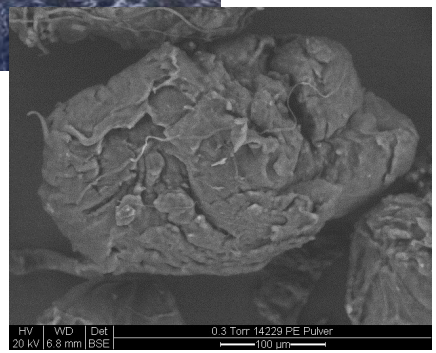
Für Mensch & Umwelt

Umwelt Bundesamt

Mikroplastik in Innenräumen: … der Weg liegt noch vor uns …

Ulrike Braun, Claus G. Bannick

Plastics in Environment



Microplastics (MP) Particles:
1 µm to 5mm, mainly polymers / synthetic macromolecules (min. 10 kDa): thermoplastics, thermosets, elastomers/rubber.

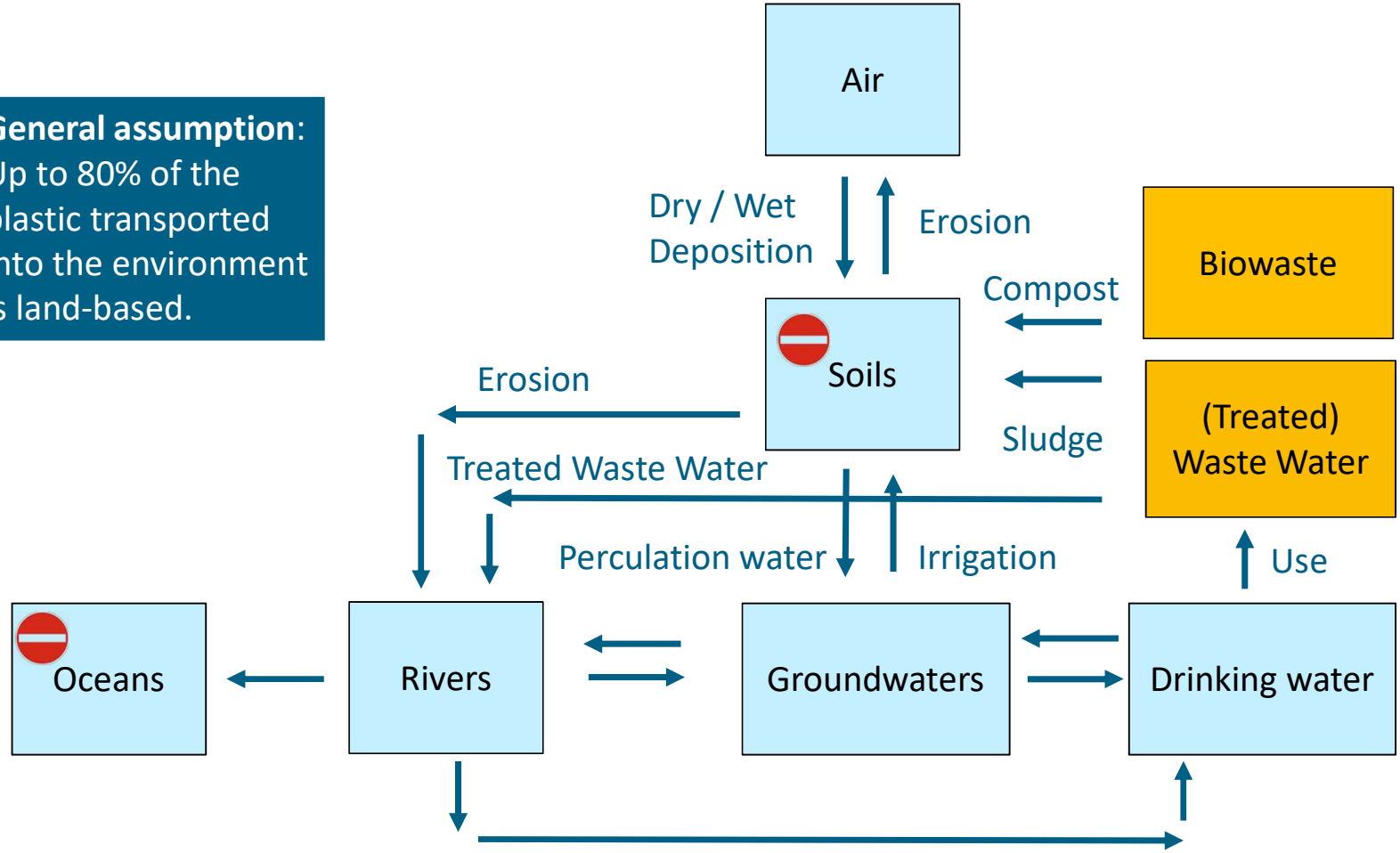
Primary MP: Additive in products (~ 0.5 k t/a)
Secondary MP: Degraded plastic products (8-12 mio t/a)

Unclear risks: pollutant sink or source, biological vector, influence on agglomeration behaviour of natural particles ????

...**No uniform analysis procedures**...

Our Task: What is the Relevance of Possible Pathways of Plastics into the Environment?

General assumption: Up to 80% of the plastic transported into the environment is land-based.



Horizonal Methods are necessary to understand relevant pathways.

fast & cost-effective
robust & validated

INDRODUCTION IN MICROPLASTIC ANALYSIS

Current microplastic research in Germany - Plastics in the environment

Eine Initiative des Bundesministeriums für Bildung und Forschung

Plastik in der Umwelt

Quellen • Senken • Lösungsansätze

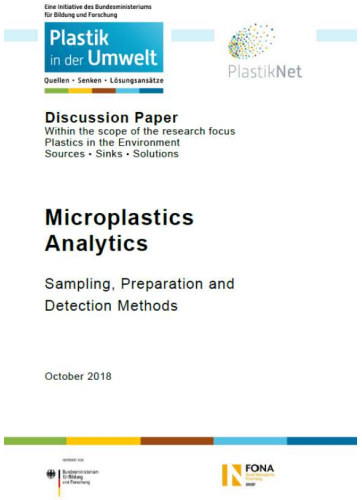
⇒ 22 consortia, ~ 40 Mio Euro, 120 institutes

⇒ Run from summer 2017 up to 2021

⇒ 12 projects are related to microplastics

⇒ Harmonization of methods

Reports with UBA guidance:



New

Report with UBA contributions:

New

Analysis of Microplastics

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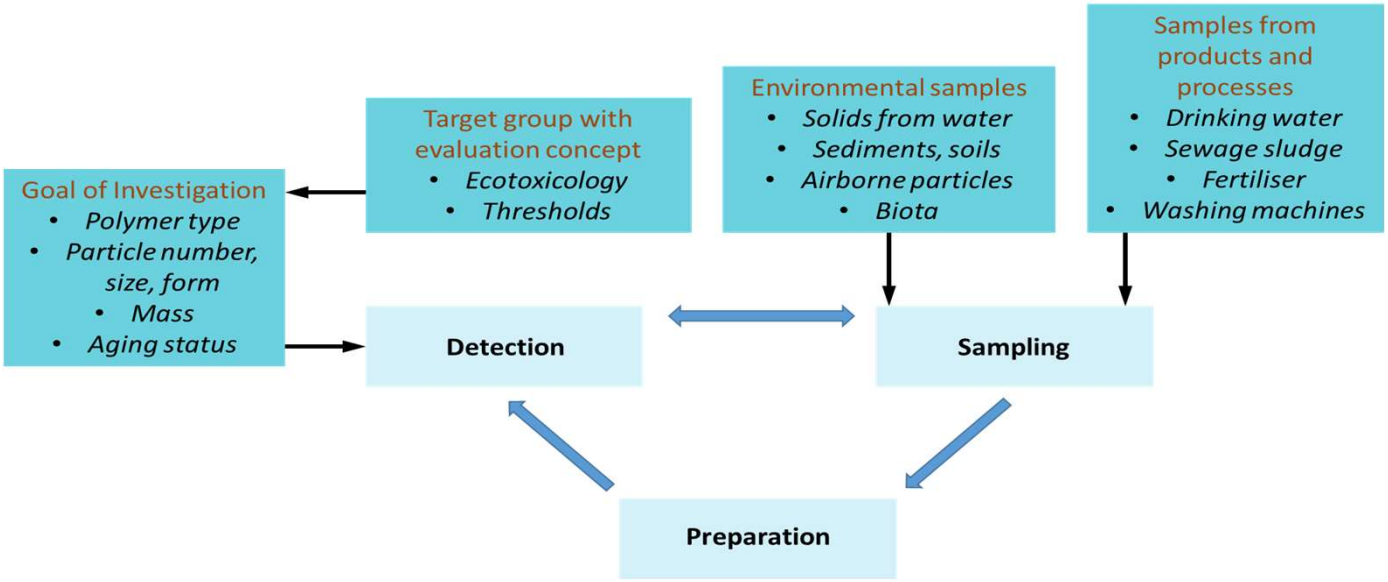
Which objective should be achieved with the measurements?

What kind of results should be achieved with the measurements?

Which environmental media / which products should be sampled?



fast & cost-effective, robust & validated,

Overview of methodical parameters for detection methods

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without consideration of the sample composition in particular

Properties	Spectroscopic						Thermoanalytical			Chemical
	µ- Raman	IR / FTIR (µ-/FPA-)	µ ATR-FTIR	ATR-FTIR	NIR	NIR Imaging	Py-GC/MS*	TED-GC/MS	DSC	ICP-MS
Sample template for measurement	Prepared filter residue	Prepared filter residue	Isolated particles	Isolated particles	Sample	Prepared filter residue	Isolated particles / prepared sample	Sample	Isolated particles / prepared sample	Sample
Maximum analyzable mass in sample	undefined	undefined	undefined	undefined	undefined	undefined	µg-mg	mg	mg	mg
Maximum particle-number per filter	$10^3 – 10^5$	$10^3 – 10^5$	undefined	undefined	undefined	$10^3 – 10^5$	undefined	undefined	undefined	undefined
Dimension measuring time (real environ. sample)	d - h	d - h	min	min	min	h - min	h	h	h	min
Lower detection limit (in practice)	1 – 5 µm	10 µm	25 – 50 µm	500 µm	~ 1 m% ***	50 µm, 5 f% ***	0.01 – 1 µg (abs)**	0.5 – 2.4 µg (abs.)**	~ 50 µg	

** Various superstructures of the pyrolysis unit (e.g. Curie point, filament, micro furnace). ** depending on polymer type and pyrolysis unit and inorganic dilution. *** m% = mass percent, f% = area percent*

Overview of result generation of the detection methods

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Properties	Spectroscopic						Thermoanalytical			Chemical
	µ Raman	IR / FTIR (µ-/FPA-)	µ ATR-FTIR	ATR-FTIR	NIR	NIR Imaging	Py-GC/MS*	TED-GC/MS	DSC	ICP-MS
Type of polymer	yes	yes	yes	yes	yes	yes	yes	yes	partially crystalline	just tires
Detectable additives	pigments	no	no	no	no	no	yes	no	no	no
Aging condition	surface oxidation	partly	surface oxidation	surface oxidation	no	no	oxidation	no	no	no
Particle number size, shape	yes	yes	yes	yes	no	yes	no	no	no	no
Contents	no	no	no	no	no	no	yes	yes	yes	yes

Our task: Monitoring / routine analysis => fast & cost-effective, robust & validated: mass contents

Overview of Exemplary Sampling Volumes

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- Representative occurrence of the feature carriers relevant to the material to be examined
- Availability of a sufficient amount of the analyte to be tested depending on the requirements of the detection method

	Raw sewage, road runoff	Treated wastewater	Surface waters	Wet deposition	Potable and ground-water	Bottled water
Volume (particle counting methods)	0.1 m^3	1 - 2 m^3	1 - 2 m^3	1 m^3	500 l	1 l
Volume (mass content methods)	0.1 m^3	1 - 2 m^3	>1 m^3	1 m^3	> 20 m^3	10 l

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Plastik in der Umwelt

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Sample Preparation

Adaptation: Real sample => Analysis sample

- Dependent on the type of sample and detection method: aspects of transport, storage, hygenisation, drying, homogenisation, fractionation / sieving
- No general specification of which sample is to be treated in which order, as this depends on the sample type and detection method
- Reduction of the organic content: acid/base, oxidative (critical for some polymers), enzymatic digestion (time consuming)
- Reduction of the inorganic content: density separation, centrifugation, elution, etc.
- Each additional step carries the risk of contamination and particle loss

No Need for TED-GC/MS

EXAMPLES USING THERMO-ANALYTICAL METHODS

Thermo-Extraction Desorption
Gas Chromatography Mass Spectroscopy (TED-GC/MS)

BAM
Bundesanstalt für Materialforschung und -prüfung

- Identification of polymers by specific decomposition products, determination of mass fractions

Gas chromatography
Mass spectrometry (GC/MS)

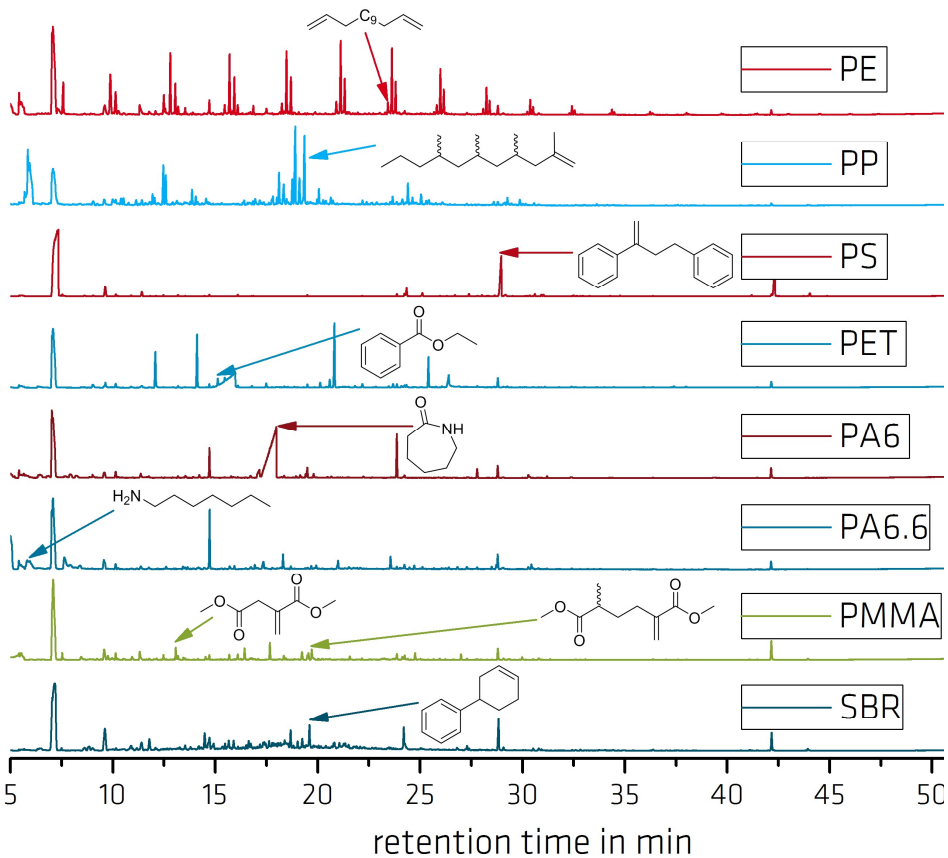
Thermogravimetric
Analysis (TGA)

Adsorber loaded with
decomposition products

Coupling devise
with solid phase adsorber

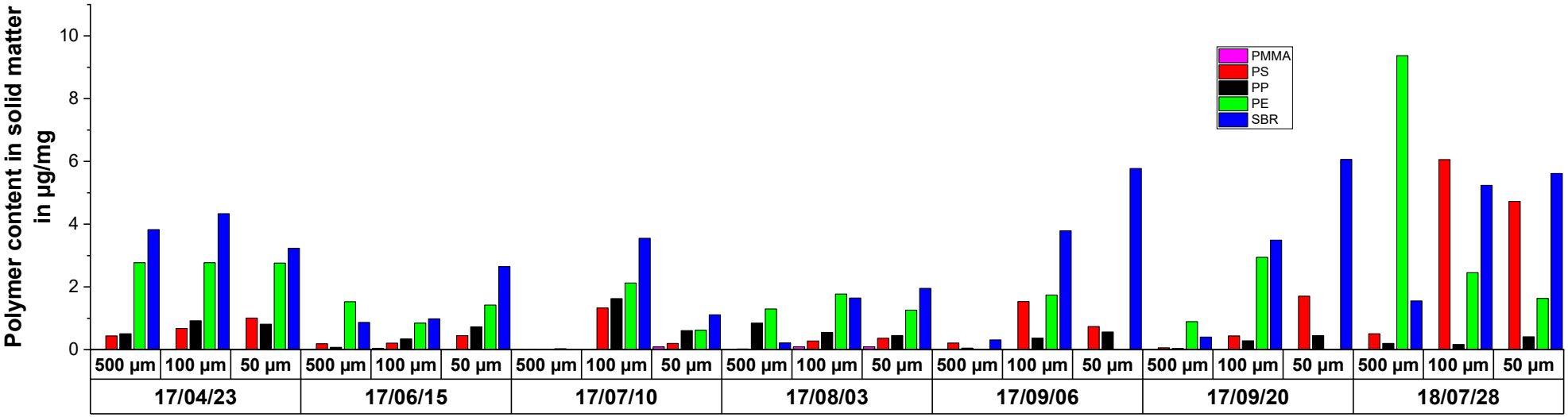
Automated thermal extraction-desorption gas chromatography mass spectrometry: A multifunctional tool for comprehensive characterization of polymers and their degradation products. Duemichen E, Eisentraut P, Celina M, Braun U. Journal of Chromatography A. 2019/05/10/;1592:133-142, 2019

TED-GC-MS: Spezifische Zersetzungsprodukt Marker



Polymer	LOD in µg (scan)
PE	2,2
PP	0,14
PS	0,08
PET	0,24
PA6	0,24
PA 6.6	3,4
PMMA	0,12
SBR	0,06

Exemplary Result: Street Run Off (Clayallee-Berlin)



- Identification PE, PP and PS
- Identification of SBR (Styrene-Butadien-Rubber) as tire abrasive marker

Two Birds with One Stone—Fast and Simultaneous Analysis of Microplastics: Microparticles Derived from Thermoplastics and Tire Wear. Eisentraut P, Dümichen E, Ruhl AS, Jekel M, Albrecht M, Gehde M, Braun U. Environmental Science & Technology Letters. 2018/10/09;5:608-613, 2018

Exemplary Result: Washing Machine Effluent

Men‘s shirt	T-shirt
	
65% CO, 35% PET	55% CO, 45% PA

+ Standard dirt
+ Standard washing powder

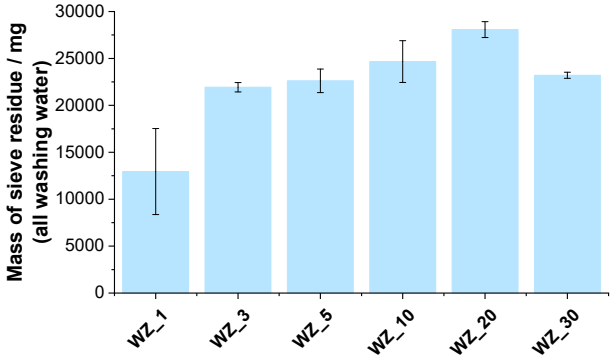
2 Machines

30x

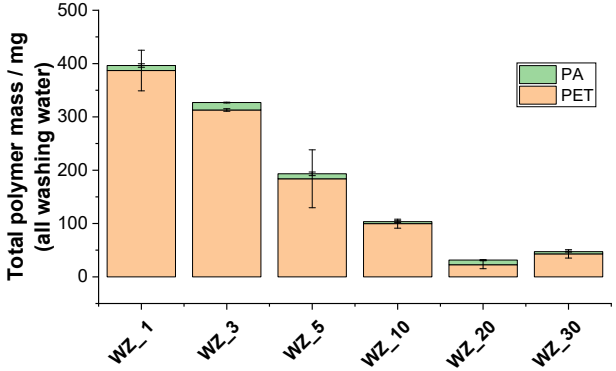
Washing parameter:
- Easy care
- Temperature: 40°C
- Max. Speed: 1200 rpm
- Load quantity: 4 kg

Sampling: Fractional filtration
Analysis: Textile physical parameters and TED-GC/MS (polymer mass)

Mass release



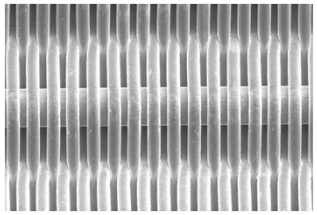
Microplastic release



PET fibre release: 0.68%.
PA fibre release: 0.03%.
→Fitrate residue mainly consists of cotton fibres, residues of dirt and washing powder.

Microplastic fibre discharge from the washing machine for realistic laundry setup, Korinna Altmann, Claus G. Bannick, Alexander Kerndorff, Claudia Heller, Monika Fuchs and Ulrike Braun, contribution on SETAC Conference 2021

Exemplary Result: Bottled Beverages



Stainless steel
(5 µm pore width)

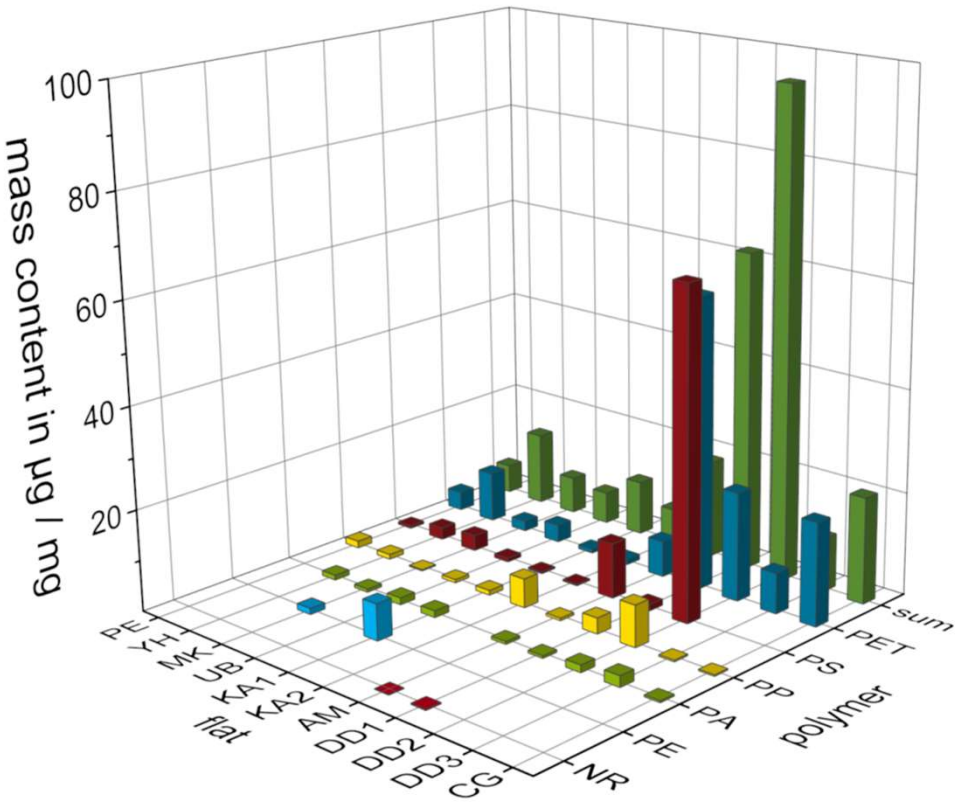
	Microplastic mass absolute / µg (9 l)	
	PE (cup)	**PET (bottle)**
Water A	(0,493)	1,738
Water B1	11,769	49,011
Water B2	-	1,731
Water B3	-	2,328
Water A, sparkling	-	(0,002)
Water B1, sparkling	-	-
Water B2, sparkling	-	--
Water B3, sparkling	-	-

- Development of a patented filter crucible for the microplastic analysis using TED-GC/MS

Smart filters for the analysis of microplastic in beverages filled in plastic bottles. Braun U, Altmann K, Herper D, Knefel M, Bednarz M, Bannick CG, Food Additives and Contaminants, 2021

THE QUESTION OF AIR MEASUREMENTS

Exemplary Results: Indoor Dusk



- Sample collected by hand (non representative)
- Identification and quantification of PET, PS, PP, PA (PE)
- Emergence of the polymers clearly different from previous samples (PET, PP, PA = fibre polymers!)

Exemplary Results: Air Filtrates on Glass Fibre Filters

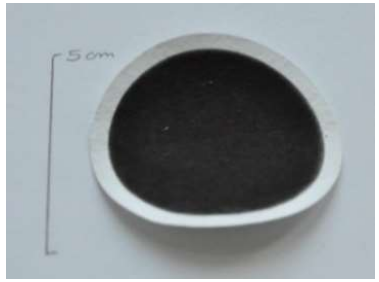
BAM
Bundesanstalt für Materialforschung und -prüfung

BAM Nr.	Probenbezeichnung	Herkunftsort
5.3/15001	AG0525_Glas-Luftfilter, unbeprobt	Referenzfilter
5.3/15002	AG0526_Glas-Luftfilter, unbeprobt	Referenzfilter
5.3/15003	AG0519_Glas-Luftfilter	Hof_1
5.3/15007	AG0521_Glas-Luftfilter	Hof_2
5.3/15044	AG0527_Glas-Luftfilter	Hof_3
5.3/15048	AG0530_Glas-Luftfilter	Hof_4
5.3/15142	AG0539_Glas-Luftfilter	Hof_5
5.3/15004	AG0520_Glas-Luftfilter	Innenraum_1
5.3/15008	AG0522_Glas-Luftfilter	Innenraum_2
5.3/15043	AG0524_Glas-Luftfilter	Innenraum_3
5.3/15139	AG0531_Glas-Luftfilter, CP 024	Innenraum_4
5.3/15009	AG0523_Glas-Luftfilter	Autobahn_1
5.3/15045	AG0528_Glas-Luftfilter	Autobahn_2
5.3/15047	AG0529_Glas-Luftfilter	Autobahn_3
5.3/15049	AG0533_Glas-Luftfilter	Autobahn_4
5.3/15140	AG0534_Glas-Luftfilter	Autobahn_5
5.3/15141	AG0535_Glas-Luftfilter	Autobahn_6
5.3/15143	AG0540_Glas-Luftfilter	Autobahn_7
5.3/15046	K0488_Glas-Luftfilter	Stadtfahrt

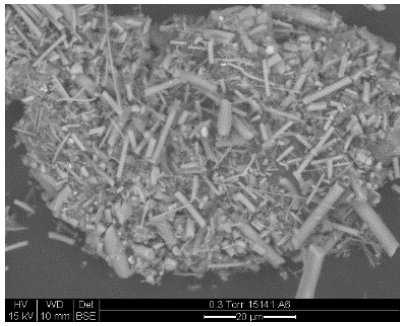
- First measurements from 2015/2016
- Courtyard, indoor air: No microplastics identified.
- Glass fibre filters are not suitable, as PS markers are always present.
- But: older device with poorer detection limit, nevertheless in the motorway samples ...

Exemplary Results: Air Filtrates on Glass Fibre Filters

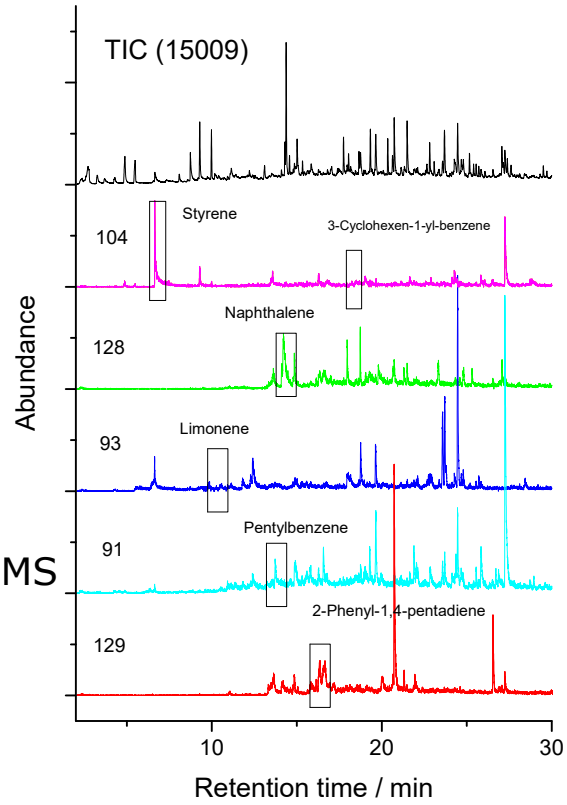
Glass-fiber filter:



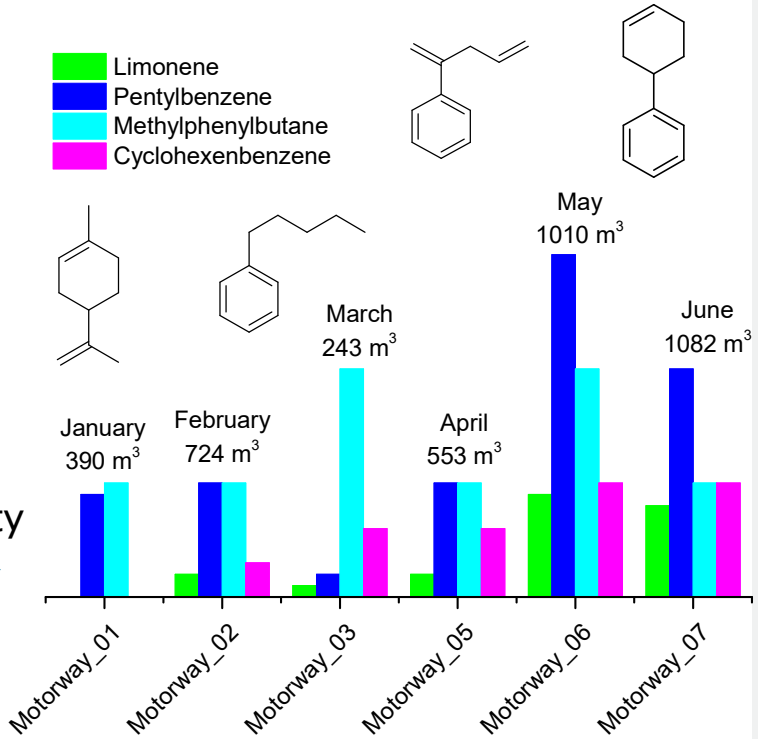
Cryo-milling



TED-GC/MS

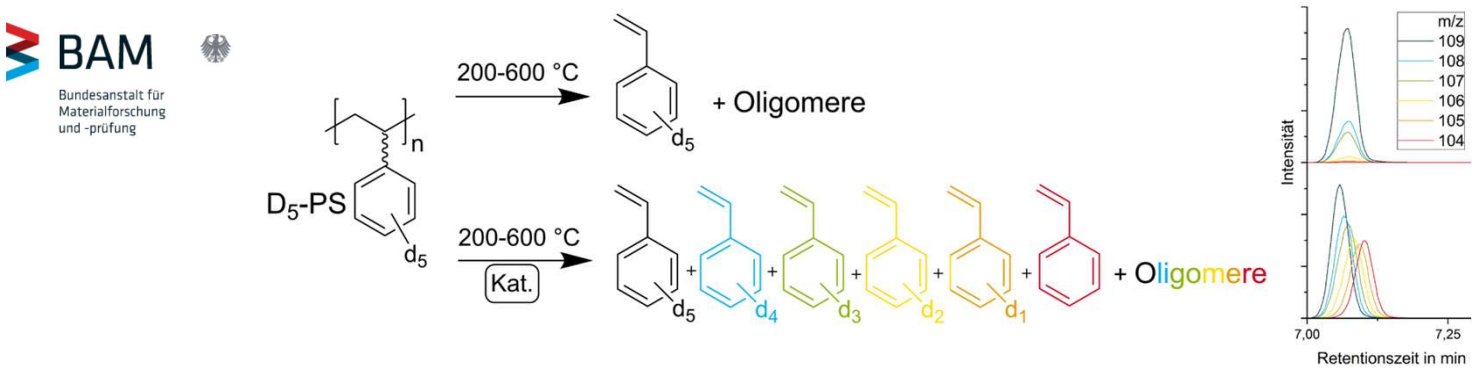


Signal Intensity



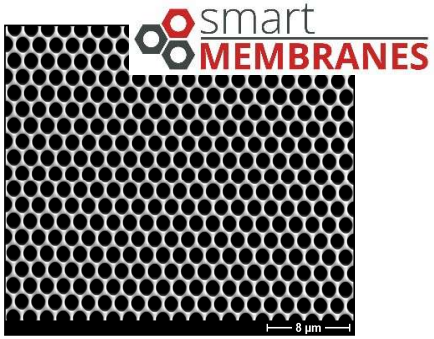
Limitation of Air Analysis: Meaningful Filter Materials

- High content of glass fibres in analysis samples
- Degradation of internal standard in presence of glass fibre: H/D exchange by catalytic reaction



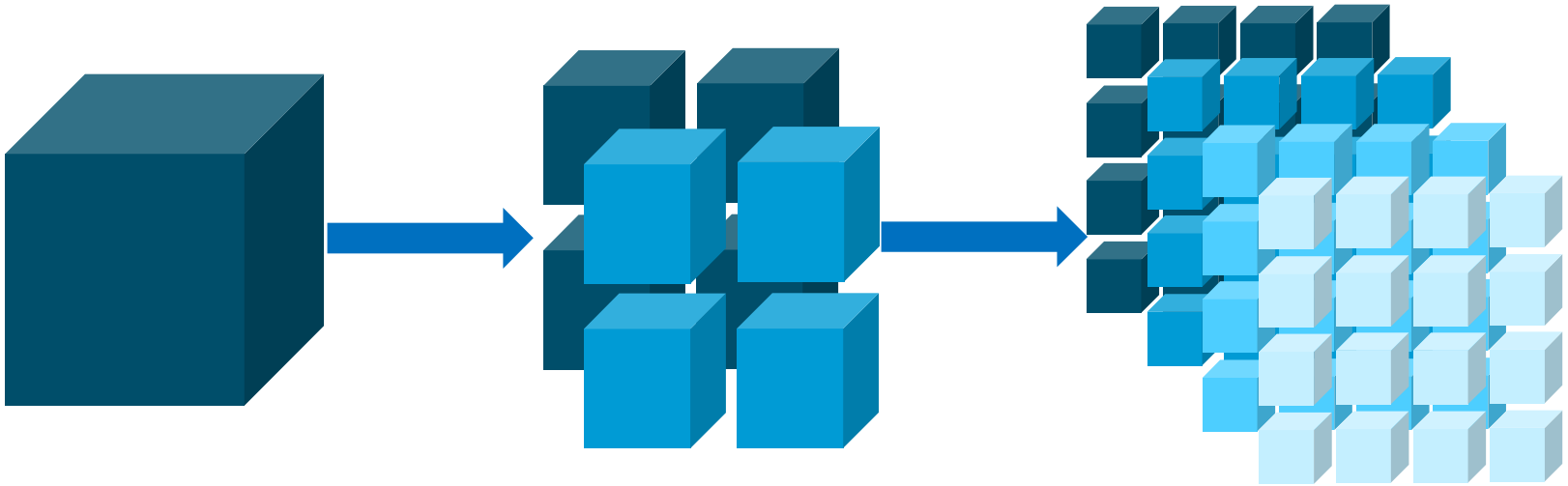
Stainless steal filters / filters crucibles and **integral MP detection** (TED-GC/MS): limitation of 5 µm

Novel filter materials: Electrochemically etched Si wafers and **imaging MP detection**



Mikroplastikanalytik mittels TED-GC/MS: H/D-Austausch an Zersetzungsprodukten von D-markiertem Polystyrol als interner Standard, P. Eisentraut, E. Dümichen, C. Goedecke, Y. Wiesner, M. Jekel, U. Braun, Contribution to Wasser Conference 2021

The Need of Imaging?
… Principle of Particle Fragmentation



- Exponentially increasing **number of particles**:
  Results of imaging techniques will be dominated by **small particles**
- Exponentially decreasing **mass of particles**:
  Results of integral techniques will be dominated by **large particles**

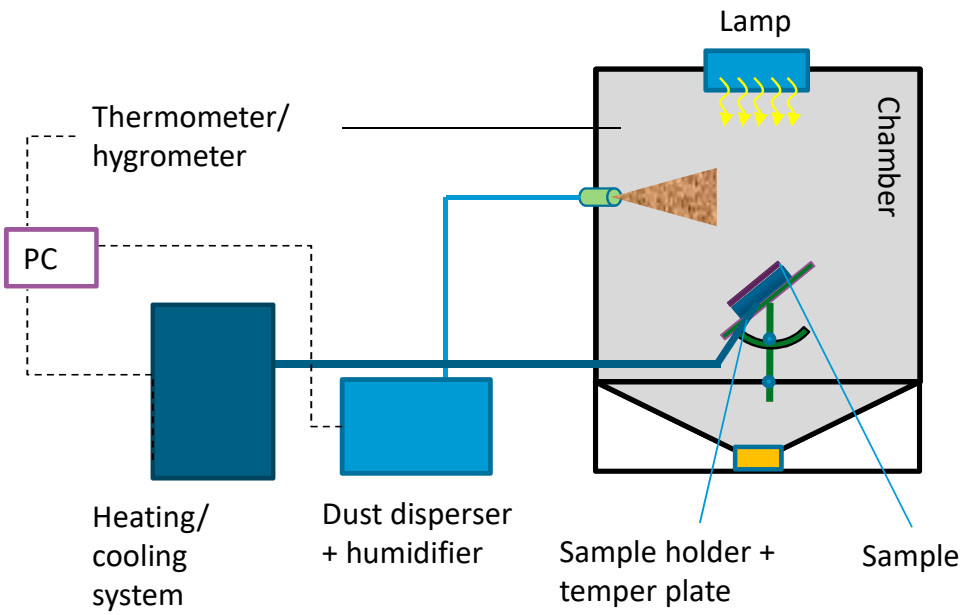
Air:
result is dominated by small particles,
high volumes need to be filtrated for mass contents
=> filters?

Laboratory dust chamber
at defined environmental condition / for filter testing

TOPAS Technologie-orientierte Partikel-, Analysen- und Sensortechnik

Fraunhofer CSP

Schematic representation of dust test setup



VDI test procedure 3956

1) Pre-dusting and chamber conditioning

2) Load samples

3) Acclimatization (sample temperature, relative humidity)

4) Injection of dust atmosphere / dust dispersion

5) Dust deposition (sedimentation)

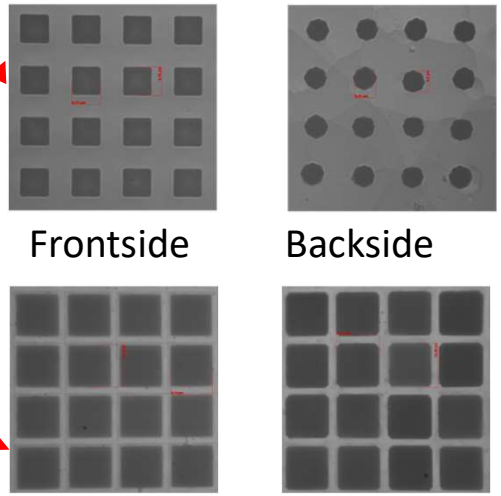
6) Unload samples

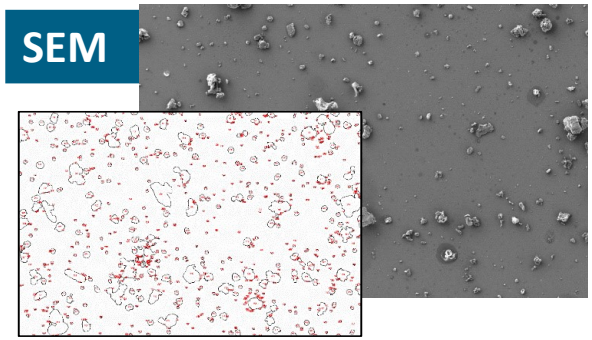
7) Sample characterization

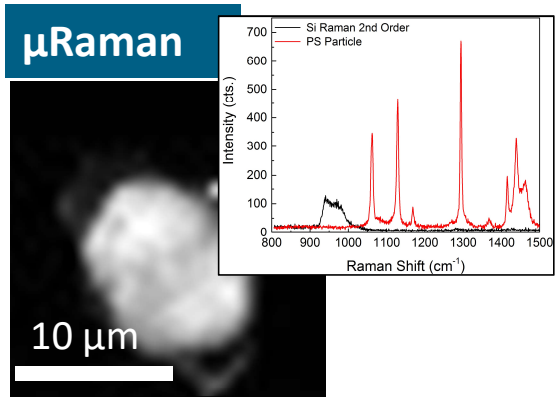
Slide: Kindly provided by CSP

Testing Filter Materials: Optimised for Subsequent Detection

Filter	Pore spacing / µm	Pore diameter / µm	Pore length / µm
SmartPor25	0,065	0,025	100
SmartPor40	0,125	0,40	100
SmartPor180	0,480	0,200	100
SmartPor180	0,480	0,400	100
MakroPor1.5	1,5	1	200
MakroPor4,2	4,2	2,5	200
MakroPor12	12	5-6	500
MakroPor12	12	9-10	500
MakroPor20	20	9-10	350
MakroPor20	20	16-18	350





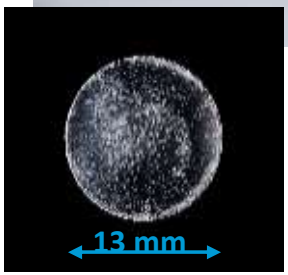


TED-GC/MS

Slide: Kindly provided by CSP

Reference Materials

@ BAM



Diluted in tablets

Available reference materials:

- all polymer sorts as pellets of mm range
- HD-PE, PVC in limited dimensions in µm range
- PS, PMMA spheres in water solutions in various dimensions of nm to µm range

- PS, PET, PA by grinding
- Aged PE by cryo-grinding

OPEN: Fibers, different polymer particles in the dimension of nm … low contents in defined matrices

ACTIVITIES IN STANDARDISATION

Plastics – Environmental Aspects – State of Knowledge and Methodologies CEN ISO/TR 21960:2020

TECHNICAL REPORT
RAPPORT TECHNIQUE
TECHNISCHER BERICHT

CEN ISO/TR 21960

March 2020

ICS 13.020.01; 83.080.01

English Version

Plastics -
Environmental aspects -
State of knowledge and methodologies (ISO/TR 21960:2020)

Plastiques -
Aspects liés à l'environnement -
État des connaissances et méthodologies
(ISO/TR 21960:2020)

Kunststoffe in der Umwelt -
Aktueller Wissensstand und Methodik
(ISO/TR 21960:2020)

This Technical Report was approved by CEN on 15 February 2020. It has been drawn up by the Technical Committee CEN/TC 249.

CEN members are the national standards bodies of Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Republic of North Macedonia, Romania, Serbia, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and United Kingdom.

1 Scope

2 Normative references

3 Terms and definitions

4 End-use applications of plastic materials and its relevance to the environment

5 Occurrence of plastics in environmental matrix and biota

6 Testing methods

7 Methodology of entry pathways (Monitoring)

8 Basics of environmental assessments

9 Recommendations for the development of standards

CEN ISO/TR 21960:2020
Terms and Definitions

nanoplastic

plastic particles smaller than 1 µm

Note 1 to entry: According to OECD nanoparticles are up to 100 nm.

microplastic

any solid plastic particle insoluble in water with any dimension between 1 µm and 1 000 µm (=1 mm)

Note 1 to entry: This term relates to plastic materials within the scope of ISO/TC 61. Rubber, fibres, cosmetic means, etc. are not within the scope.
Note 2 to entry: Typically, a microplastic object represents a particle intentionally added to end-user products, such as cosmetic means, coatings, paints, etc. A microplastic object can also result as a fragment of the respective article.
Note 3 to entry: Microplastics may show various shapes.
Note 4 to entry: The defined dimension is related to the longest distance of the particle.

large microplastic

any solid plastic particle insoluble in water with any dimension between 1 mm and 5 mm

Note 1 to entry: *Microplastics* (3.9) may show various shapes.
Note 2 to entry: Typically, a large microplastic object represents an article consisting of plastic or a part of an end-user product or a fragment of the respective article.
Note 3 to entry: Microplastics in this size range are, for example, plastic pellets as intermediates for further down-stream processing such as moulding, extrusion, etc. resulting to semi-finished products which are not final end-user products.

macroplastic

any solid plastic particle or object insoluble in water with any dimension above 5 mm

Note 1 to entry: Typically, a macroplastic object represents an article consisting of plastic or a part of an end-user product or a fragment of the respective article, such as cups, cup covers.
Note 2 to entry: The defined dimension is related to the longest distance of the particle.

Principles for plastic and microplastic analysis present in the environment ISO/CD 24187.2:2021

ISO/CD 24187.2:2021

ISO TC 61/SC 14/WG 4

Secretariat: DIN

Principles for the analysis of plastic and microplastic present in the environment

CD stage

Warning for WDs and CDs

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Recipients of this draft are invited to submit, with their comments, notification of any relevant patent rights of which they are aware and to provide supporting documentation.

Eine Initiative des Bundesministeriums für Bildung und Forschung

Plastik in der Umwelt

Quellen • Senken • Lösungsansätze

General requirements for all analytical steps

Identification of appropriate detection methods

Sampling
- Water
- Terrestric, semiterrestric and subhydric soils
- Air
- Sludges, other organic materials, mineral material
- Biota

Sample preparation
- Drying, milling and grinding
- Removal of inorganic matter
- Removal of organic matter

Detection
- Methods for determining particle number and sizes (spectroscopic procedures)
- Methods for determining mass content (thermo-analytical and chemical methods)
- Evaluating data processing approaches

Aspects of metrology and testing

Activities in Standardisation

ISO/TC 61/SC 14 „Plastics“	ISO/TC 147/SC 2 „Water quality“
Plastics in the Environment — State of knowledge and Methodologies (ISO/TR 21960) Principles for the development of standards for investigation procedures of plastics in environmental matrices and related materials	
ISO/TC 147/SC 2/JWG 1 **“Plastics (including microplastics) in waters and related matrices"**	
Water quality — Analysis of microplastics — Part 1: General and sampling, Part 2: Methods using vibrational spectroscopy in drinking water and groundwater, Part 3: Thermoanalytical methods in waters with low content of natural suspended solids, Part 4: Effect based methods, Part 5: Sample preparation	

Activities in Standardisation

ISO/TC 61/SC 14 „Plastics“	ISO/TC 147/SC 2 „Water quality“
Plastics in the Environment — State of knowledge and	
ISO/TC 147/SC 2/JWG 1 **“Plastics (including microplastics) in waters and related matrices"**	
Water quality — Analysis of microplastics — Part 1: General and sampling, Part 2: Methods using vibrational spectroscopy in drinking water and groundwater, Part 3: Thermoanalytical methods in waters with low content of natural suspended solids, Part 4: Effect based methods, Part 5: Sample preparation	

ISO/TC 147/SC 6 (Sampling)

ASTM (WK 67788, 70831, 67565)

DIN-NAL (Food Products)

ISO/TC 38 (Textiles)

ISO/TC 190 (Soil Quality)

…

Summary and Outlook

- Microplastic analysis: complex task of sampling, sample preparation, detection.
- Fast routine analytics for microplastic determination in waters is available using fractionated filtration and TED-GC/MS.
- Fast measurements is needed for high throughput of various samples:
  => Identification of sources, transport and fate of microplastic in future
  => Recommendation for relevant avoiding strategies.

- Monitoring of atmospheric samples / indoor air: still at beginning - challenging because of missing routine filtration procedures with subsequent detection for small particles with low masses

- Harmonisation for Microplastic analysis is (nearly) available: definitions, general aspects and recommendation, …
- Harmonisation for bottled water is running:
  => Water quality — Analysis of microplastics — Part 1: General and sampling, Part 2: Methods using vibrational spectroscopy in drinking water and groundwater, Part 3: Thermoanalytical methods in waters with low content of natural suspended solids,

Umwelt Bundesamt

Thank You!
Thank You to Team UBA!

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Eine Initiative des Bundesministeriums für Bildung und Forschung
Plastik in der Umwelt
Quellen • Senken • Lösungsansätze

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