Quantitative ^{1}H-NMR Spectroscopy as an Efficient Method for Identification and Quantification of PVC, ABS and PA Microparticles

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Supporting Information:

Table SI 1	(2)	Possible solvents for PVC, ABS and PA based on the literature. Given are the solvents already described for NMR spectroscopic investigations of the respective polymers, the corresponding ^{1}H-Signals of the polymers and the residual proton signals in ppm as well as the solvents tested in this survey.
Figure SI 1	(2)	^{1}H-NMR spectra of matrix effects of natural aquatic biofilm. **a**) ~11 mg/mL biofilm solved in $CDCl_3$/FA 3:2. **b**) ~16 mg/mL biofilm solved in $CDCl_3$. **c**) ~14 mg/mL biofilm solved in DMSO-d6.
Figure SI 2	(2)	^{1}H-NMR spectrum of PVC after line fitting for the PF-method in the range of 3.0-1.5 ppm. Blue represent the individual fitted peaks and pink represent the sum of the fitted peaks.
Figure SI 3	(3)	^{1}H-NMR spectra of ABS in $CDCl_3$ (left) and in DMSO-d6 (right) after line fitting for the PF-method in the range of 8.0-6.0 ppm and 3.0-2.0 ppm. Blue represent the fitted peaks and pink represent the sum of the fitted peaks. ^{1}H NMR spectrum of ABS after line fitting for the PF-method in the range of 8.0-6.0 ppm. Blue represent the individual fitted peaks and pink represent the sum of the fitted peaks.
Figure SI 4	(3)	Calibration curves for the signal which can also be used for quantification for the MP particles of PVC, ABS and PA with the appropriate confidence interval (CI). Plotted is the MP concentration in mg/mL against the normalized intensity.
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Table SI 4	(5)	Overview of the ^{1}H-Signals of the MP polymer types, residual sovlent signals and matrix effects of biofilm in the corresponding solvent conditions.

***Table SI 1**. Possible solvents for PVC, ABS and PA based on the literature. Given are the solvents already described for NMR spectroscopic investigations of the respective polymers, the corresponding ^{1}H-Signals of the polymers and the residual proton signals in ppm as well as the solvents tested in this survey.*

MP	Solvents used in the literature	MP ^{1}H signals in ppm	Solvent ^{1}H signals in ppm	Solvents tested in this survey
PVC	DMSO [28] $CDCl_3$ [27]	4.7-4.3; 2.4-2.1 [28] 4.45; 2.1 [27]	2.5 7.2	DMSO
ABS	$CDCl_3$ [30] DMSO [29]	7.2-6.4; 5.5; 2.5-1.2[30] 7.2-6.8; 5.3; 2.5-1.4 [29]	7.2 2.5	$CDCl_3$ DMSO
PA 6.6	TFA[31] Cresol/ODCB [26]	3.3; 2.5; 1.7, 1.3 [31] not specified [26]	~ 12 7.2; 6.6; 5.0; 2.3	$CDCl_3$/FA 3:2

TFA, trifluoroacetic acid; *FA*, formic acid; *ODCB*, 1,2-dichlorobenzene.

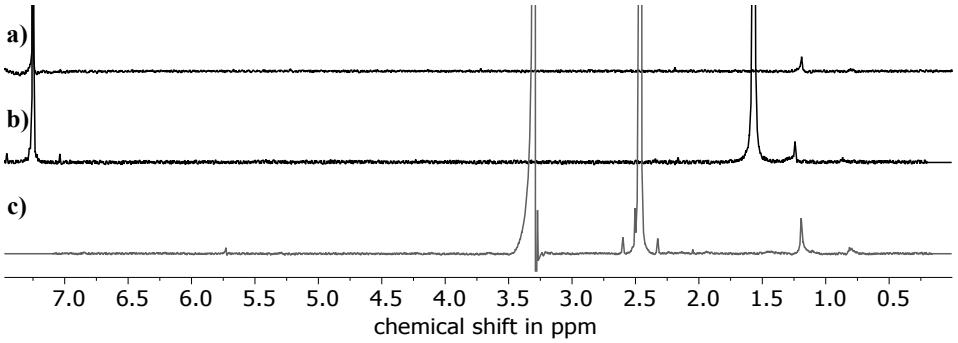

***Figure SI 1** ^{1}H-NMR spectra of matrix effects of natural aquatic biofilm in the respective deuterated solvent. **a)** ~11 mg/mL biofilm solved in $CDCl_3$/FA 3:2. **b)** ~16 mg/mL biofilm solved in $CDCl_3$. **c)** ~14 mg/mL biofilm solved in DMSO-d6. Aquatic biofilm, i.e. a complex and dynamic community of algae, cyanobacteria, heterotrophic microorganisms, and detritus attached to surfaces in most aquatic exosystems. Biofilm samples were collected at the river Moselle (position 50° 21' 49.8" N 7° 33' 54.6" E) by brushing light-exposed grown surfaces of submerges stones and and dried at 60° C.*

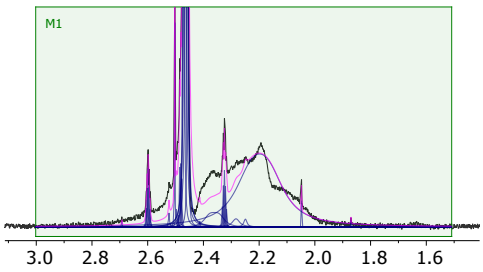

***Figure SI 2** ^{1}H-NMR spectrum of PVC after line fitting for the PF-method in the range of 3.0-1.5 ppm. Blue represent the fitted peaks and pink represent the sum of the fitted peaks.*

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We here refer to aquatic biofilm (i.e. stream periphyton) which is a complex and dynamic community of algae, cyanobacteria, heterotrophic microorganisms, and detritus. Under natural conditions, bacteria generally exist in the biofilm state, i.e. cells attached to each other and also to a surface, embedded in a protective matrix. In aquatic ecosystems aquatic biofilm represents an important food source for grazing macroinvertebrates or fish habitats and can adsorb contaminants from the free-flowing water.

Analyzed biofilm samples were taken from natural biofilm of the river Moselle (at position 50° 21′ 49.8″ N 7° 33′ 54.6″ E) by brushing grown surfaces (i.e. stones), as is it not commercially available.

Relevant information on the general composition of biofilm and the collection site was added to the caption of figure SI 2.

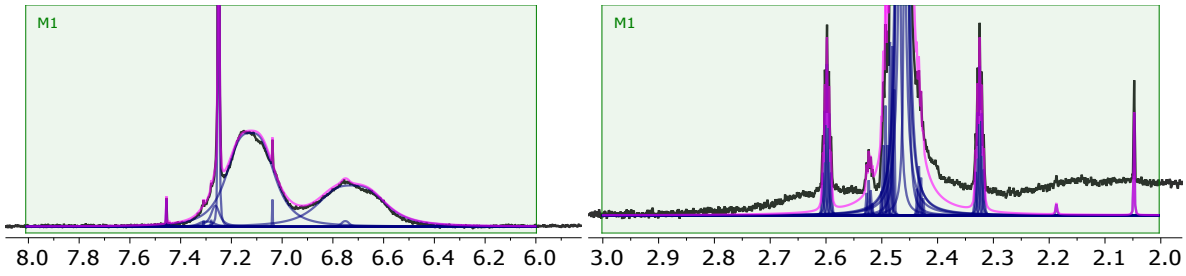

Figure SI 3 *^{1}H-NMR spectra of ABS in $CDCl_3$ (left) and in DMSO-d6 (right) after line fitting for the PF-method in the range of 8.0-6.0 ppm and 3.0-2.0 ppm. Blue represent the fitted peaks and pink represent the sum of the fitted peaks.*

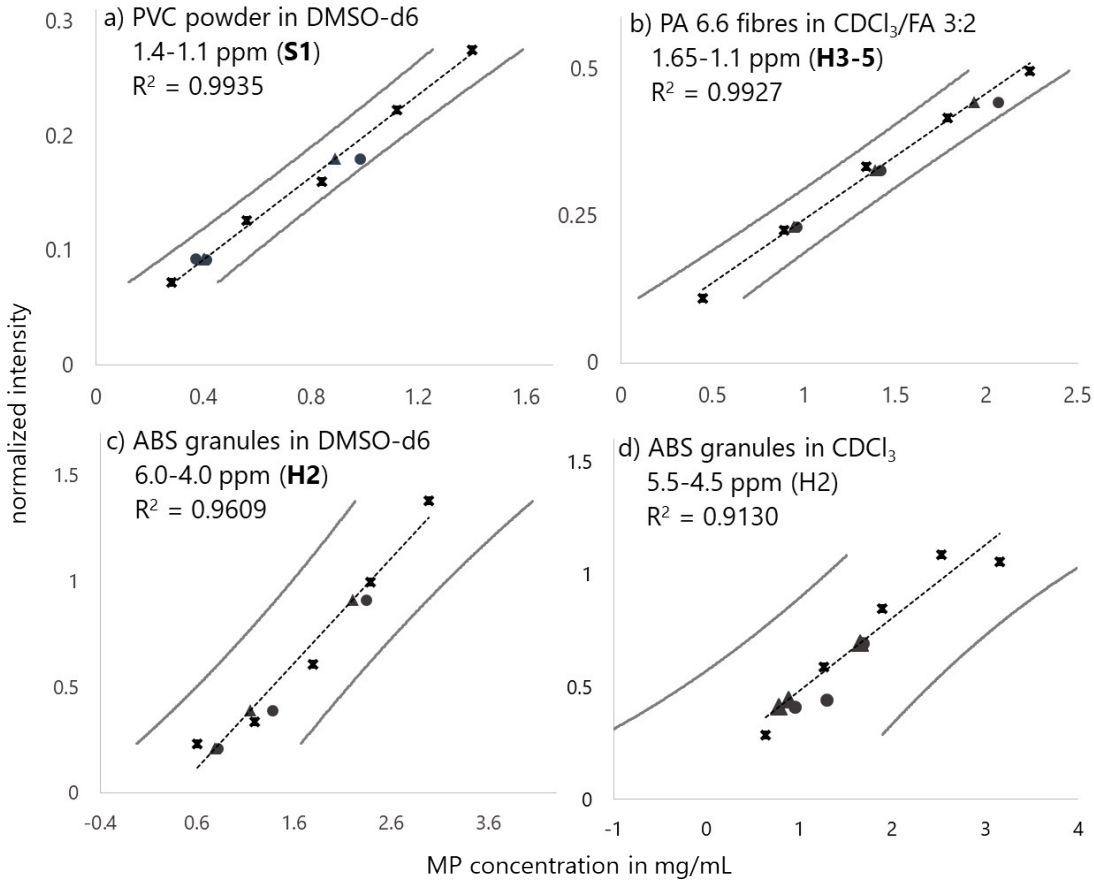

Figure SI 4. *Calibration curves for the signal which can also be used for quantification for the MP particles of PVC, ABS and PA with the appropriate confidence interval (CI). Plotted is the MP concentration in mg/mL against the normalized intensity. In addition, the true and calculated values of the model samples are given. a) signal range of 1.4-1.1 ppm (S1) for PVC particles, b) signal range of 1.65-1.1 ppm (H3-5) for PA fibres, c) signal range of 6.0-4.0 ppm (H2) for ABS particles in DMSO-d6 and d) signal range of 5.5-4.5 ppm (H2) for ABS particles in CDCl3 are compared. For linearity data see supporting information SI 6.*

Table SI 2. *Linearity data of MP particles (PVC, ABS and PA). Data were calculated from five measurement points. PVC: Integration area 4.7-4.05 ppm (H1) and 1.4-1.1 ppm (S1). For integration the peak-fitting method was used. 0.28-1.40 mg/mL concentration range. ABS in $CDCl_3$: Integration area 7.1-6.0 ppm (H1) and 5.5-4.5 ppm (H2) are given. For integration the peak-fitting method was used. 0.63-3.15 mg/mL concentration range. ABS in DMSO-d6: Integration area 7.5-6.0 ppm (H1) and 6.0-4.0 ppm (H2) are given. For integration the peak-fitting method was used. 0.63-3.15 mg/mL concentration range.PA: Integration area 3.2-3.05 ppm (H1) and 1.65-1.1 ppm (H3-5) are given. For integration the peak-fitting method was used. 0.45-2.24 mg/mL concentration range.*

	MP particles	Slope ± SD	Intercept ± SD	R^2
Signal H1	PVC in DMSO-d6	1.3487 ± 0.0330	- 0.0455 ± 0.0306	0.9982
Signal H1	ABS in $CDCl_3$	3.8863 ± 0.2247	+ 0.6164 ± 0.4699	0.9901
Signal H1	ABS in DMSO-d6	3.8158 ± 0.0312	+ 0.0832 ± 0.0617	0.9998
Signal H1	PA in $CDCl_3$/FA	0.0714 ± 0.0029	+ 0.0106 ± 0.0043	0.9950
Signal S1	PVC in DMSO-d6	0.1797 ± 0.0084	+ 0.0204 ± 0.0078	0.9935
Signal H2	ABS in $CDCl_3$	0.3235 ± 0.0577	+ 0.1609 ± 0.1206	0.9130
Signal H2	ABS in DMSO-d6	0.4960 ± 0.0578	- 0.1774 ± 0.1143	0.9609
Signal H3-5	PA in $CDCl_3$/FA	0.2156 ± 0.0107	+ 0.0281 ± 0.0158	0.9927

Table SI 3. *Quantitative results for model samples using the signal which can also be used for quantification for the MP particles of PVC, ABS and PA. True Value ± weighting error and calculated values ± confidence interval (CI) of the respective MP samples in mg/mL as well as the accuracy (bias in %) and precision (RSP in %) are given. PVC samples: integration area 1.4-1.1 ppm (S1). For integration the PF-method was used. ABS samples in DMSO-d6: integration area 6.0-4.0 ppm (H2). For integration the PF-method was used. ABS samples in CDCl3: integration area 5.5-4.55 ppm (H2). For integration the PF-method was used. PA samples: integration area 1.65-1.1 ppm (H3-5). For integration the INT-method was used.*

	MP signal	True Value ± Δx (mg/mL)	Calculated ± CI (mg/mL)	Accuracy (bias in %)	Precision (RSD in %)
PVC 1 (in DMSO-d6)	S1	0.98 ± 0.01	0.94 ± 0.13	95.5	99.9
PVC 2 (in DMSO-d6)	S1	0.78 ± 0.01	0.68 ± 0.13	87.2	99.9
PVC 3 (in DMSO-d6)	S1	0.41 ± 0.01	0.44 ± 0.14	107	99.9
ABS 1 (in DMSO-d6)	H2	2.34 ± 0.01	2.18 ± 0.78	93.0	99.2
ABS 2 (in DMSO-d6)	H2	1.37 ± 0.01	1.15 ± 0.80	84.3	99.2
ABS 3 (in DMSO-d6)	H2	0.81 ± 0.01	0.78 ± 0.85	95.9	99.8
ABS 1 (in $CDCl_3$)	H2	1.68 ± 0.01	1.70 ± 1.25	101	99.9
ABS 2 (in $CDCl_3$)	H2	1.29 ± 0.01	0.88 ± 1.37	68.1	99.9
ABS 3 (in $CDCl_3$)	H2	0.95 ± 0.01	0.70 ± 1.39	73.4	92.2
PA 1 (in $CDCl_3$/FA 3:2)	H3-5	2.06 ± 0.01	1.94 ± 0.26	94.1	99.2
PA 2 (in $CDCl_3$/FA 3:2)	H3-5	1.42 ± 0.01	1.39 ± 0.24	97.9	99.9
PA 3 (in $CDCl_3$/FA 3:2)	H3-5	0.96 ± 0.01	0.95 ± 0.25	98.6	99.9

Table SI 4. *Overview of the ^{1}H-Signals of the MP polymer types, residual sovlent signals and matrix effects of biofilm in the corresponding solvent conditions. Indicated are the ^{1}H-signals or the range of the chemical shift in ppm, whether the MP signals is suitable for quantitative analysis by qNMR and the reasons why the corresponding signal is not suitable.*

		Signals [ppm]	**Suitable qNMR**	**Reasons why not suitable for quantification**
DMSO-d6	solvent	2.47-2.4 (DMSO) 3.36-3.24 (H_2O)		
	matrix	2.3-1.9; 1.5-0.6		
	PVC	4.6-4.2 (H1)	yes	-
		2.5-2.1 (H2)	no	Signal overlap with solvent signal, interference with matrix effects possible
		1.4-1.1 (S1)	(yes)	intereference with matrix effects possible
		0.9-0.7 (S2)	no	interference with matrix effects possible, low signal intensity
	ABS	7.7-6.5 (H1)	yes	-
		5.9-4.5 (H2)	(yes)	Low signal intensity
		2.7-1.2 (H3-H7)	no	Signal overlap with solvent signal, Interference with matrix effects possible
		0.9-0.7 (H8)	no	Interference with matrix effects possible, low signal intensity
$CDCl_3$	solvent	7.25 ($CDCl_3$)		
	matrix	1.6-0.6		
	ABS	7.4-6.3 (H1)	(yes)	Signal overlap with solvent signal
		5.8-4.7 (H2)	(yes)	low signal intensity
		3.0-1.0 (H3-H7)	(yes)	Intereference with matrix effects possible
		0.9-0.7 (H8)	no	Interference with matrix effects possible, low signal intensity
$CDCl_3$/FA	solvent	7.25 ($CDCl_3$)		
	Matrix	1.4-0.6		
	PA 6.6	3.2-3.0 (H1)	yes	-
		2.3-2.15 (H2)	(yes)	interference with matrix effects possible
		1.65-1.1 (H3-H5)	(yes)	interference with matrix effects possible
		7.31 (amines)	(yes)	low signal intenity