Electronic Supplementary Material (ESI) for Analytical Methods.

Electronic Supplementary Information

Optimisation of an extraction/leaching procedure for the characterization and quantification of titanium dioxide (TiO_2) nanoparticles in the aquatic environment using SdFFF-ICP-MS and SEM EDX analysis.

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<u>Used equations</u>

Calculation of the Settling time (t_s) for the size cut-off using a centrifuge

$$t_s = \ln\left(\frac{r_{out}}{r_{in}}\right)\frac{18\,\eta}{4\pi^2 \Delta p d^2 \left(\frac{rpm}{60}\right)^2} \qquad \text{(ESI 1)}$$

t_s: settling time (min)
r_{out}: outer diameter of the centrifuge tube (cm)
r_{in}: inner diameter of the centrifuge tube (cm)
η: viscosity kg/(s·m)
Δρ: delta density (water and TiO_2, kg/m^3)
rpm: rounds per min
d: diameter of the particles (m)

Calculation of the particle size distribution

The following equations have been used to perform different calculations related with the analysis of nano particles via SdFFF. The SdFFF theoretical basis for the conversion of retention time data into size distribution is described in detail elsewhere.[1,2] Briefly, the retention ratio R obtained experimentally by SdFFF is a function of the layer thickness λ:

$$R = \frac{t_0}{t_r} = 6\lambda\left[coth\left(\frac{1}{2\lambda}\right) - 2\lambda\right] \qquad \text{(ESI 2)}$$

Being t_0 the void time and t_r the retention time.

In SdFFF, the layer thickness λ is expressed as:

$$\lambda = \frac{kT}{m\omega^2 rw} \qquad \text{(ESI 3)}$$

k the Boltzmann constant
T the absolute temperature in K
w the channel thickness (m)

ω the angular velocity

r the radius of the centrifuge from rotation axis to the channel (m).

m mass of the particle

t_r retention time (min)

The particle size can be calculated from the retention time obtaining a size distribution profile by applying the equation:

$$d = \left[\left(\frac{6kT}{\pi G w \Delta\rho t_0}\right) t_r\right]^{1/3} \qquad \text{(ESI 4)}$$

d the diameter of the particles according to FFF theory

k the Boltzmann constant

T the absolute temperature in K

w the channel thickness (m)

t_0 void time (min)

r the radius of the centrifuge from rotation axis to the channel (m)

t_r retention time (min)

G the centrifugal acceleration

$\Delta\rho$ the difference between the density of the particle and the one of the carrier liquid.

Tables

ESI Table 1 Detailed information related with the different sampling sites

Sample name	Sampling date	Air- / Water temperature (°C)	pH-Value	Conductivity (µS/cm)
December 2016 (west)	20.12.2016	3 / 5.2	7.83	673
December 2016 (south)	20.12.2016	2 / 5.3	7.68	699
September 2016 (west)	23.09.2016	17 / 19.6	8.15	690
September 2016 (south)	23.09.2016	12 / 19.6	8.06	689
June 2016 (west)	01.06.2016	24 / 19.2	8.08	684
June 2016 (south)	01.06.2016	21 / 19.1	7.98	685
June 2015 (west)	01.06.2015	22 / 18.5	8.14	674

June 2015 (south)	01.06.2015	20 / 18.5	8.09	677

ESI Table 2 Instrumental parameters used for the operation of SdFFF (CF2000, PostNova Analytics) and ICP-MS/MS (Agilent 8800, Agilent Technologies) coupling

SdFFF

Tip to tip channel length	89.5 cm
Channel breadth	2.1 cm
Channel Thickness (*w*)	0.0231 cm
Injection volume	21.54 µL
Void volume (V^0)	2.0 mL
Relaxation time	5 min
Channel flow rate	0.5 mL/min
Initial rotation speed	2500 rpm
Power field programming	t_1 = 8 min (focus time at the initial field), and t_a = -64 (field decay parameter)
Final field	100 rpm
Carrier solution	0.15 mmol/L NaOH

ICP-MS/MS

RF-Power	1600 W
Torch/Injector	Quartz/Quartz
Spray chamber	Quartz
Sampler and skimmer cones	Cu-Ni, Ni
Carrier gas flow	1.12 L/min
Makeup gas flow	0.11 L/min
Cell gas flow rate (He)	4.5 mL/min
Q1 bias	-2 V
Qctopole bias	-5 V
Dwell times	0.3 s
Tuning solution	10 µg/L (Li, Y, Tl, Ce in 2 % (*w*/*w*) HNO_3)

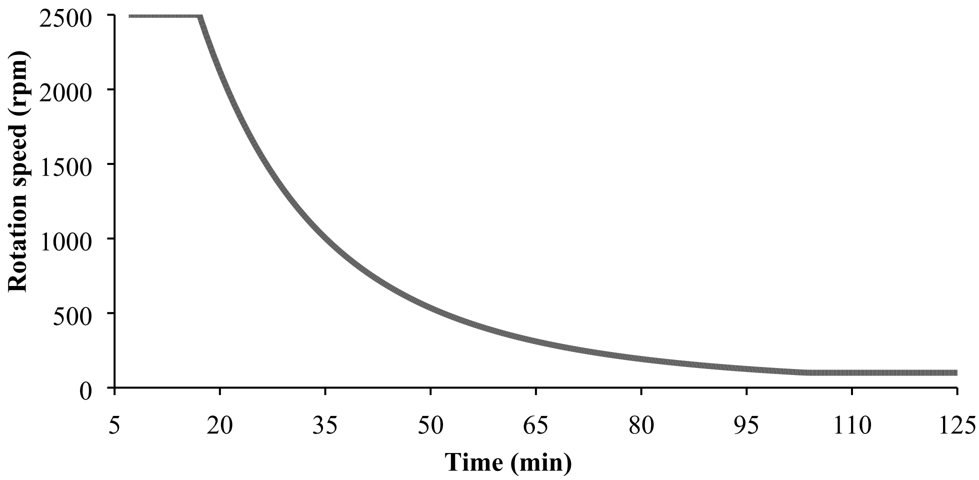
ESI Table 3 Details of the used microwave assisted acid digestion power, temperature and time program

Energy / Temperature	Time
1600 W / 180 °C	60 min
1600 W / 180 °C	180 min
1600 W / 180 °C	60 min

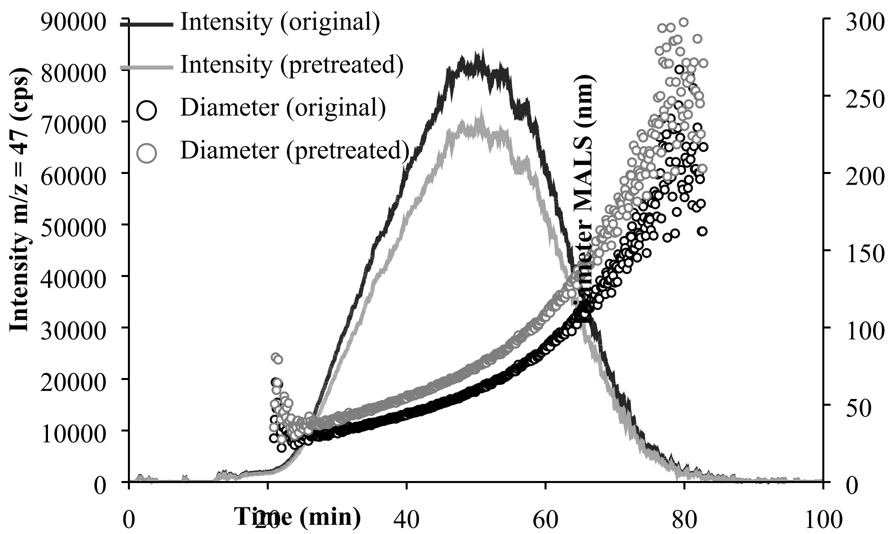
ESI Table 4 Instrumental parameter used during the measurement of the sediment digests via ICP-MS/MS (Agilent 8800, Agilent Technologies)

ICP-MS/MS	
RF-Power	1550 W
Torch/Injector	Quartz/Saphire
Spray chamber	PFA
Sampler and skimmer cones	Cu-Ni, Ni
Carrier gas flow	1.12 L/min
Makeup gas flow	0.11 L/min
Cell gas flow rate (H_2,He,O_2)	6 mL/min, 4.5 mL/min, 2.5 mL/min (30 %)
Q1 bias	-2 V
Qctopole bias	-5 V
Dwell times	0.3 s
Tuning solution	10 µg/L (Li, Y, Tl, Ce in 2 % (*w*/*w*) HNO_3)

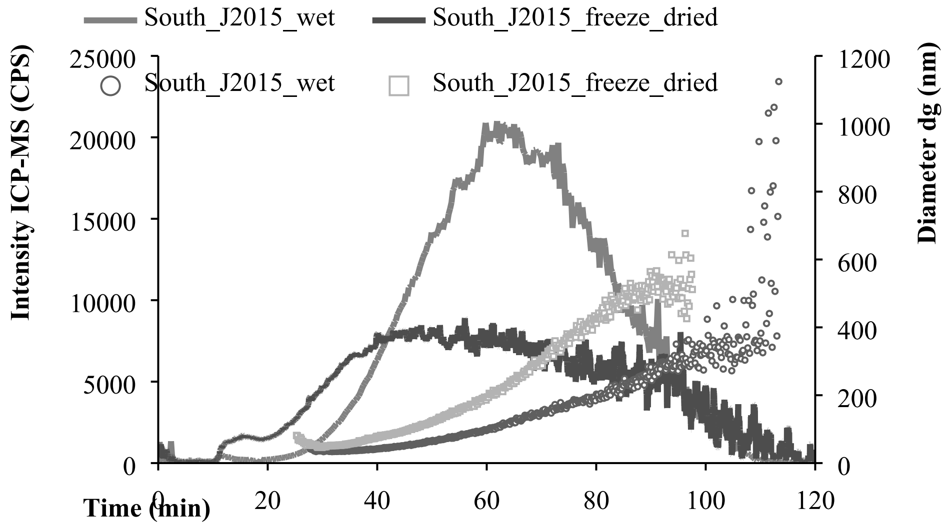
Figures



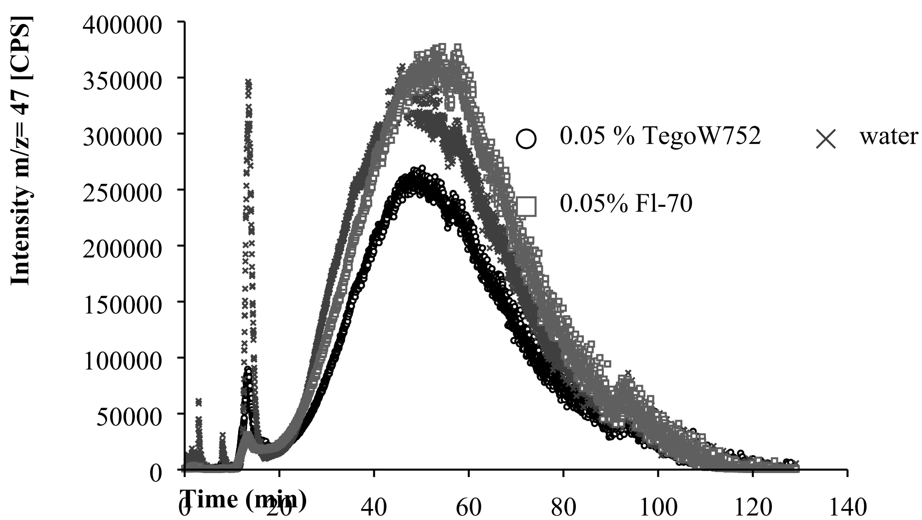
ESI Figure 1 Decay program used for the separation of the particles with the SdFFF system



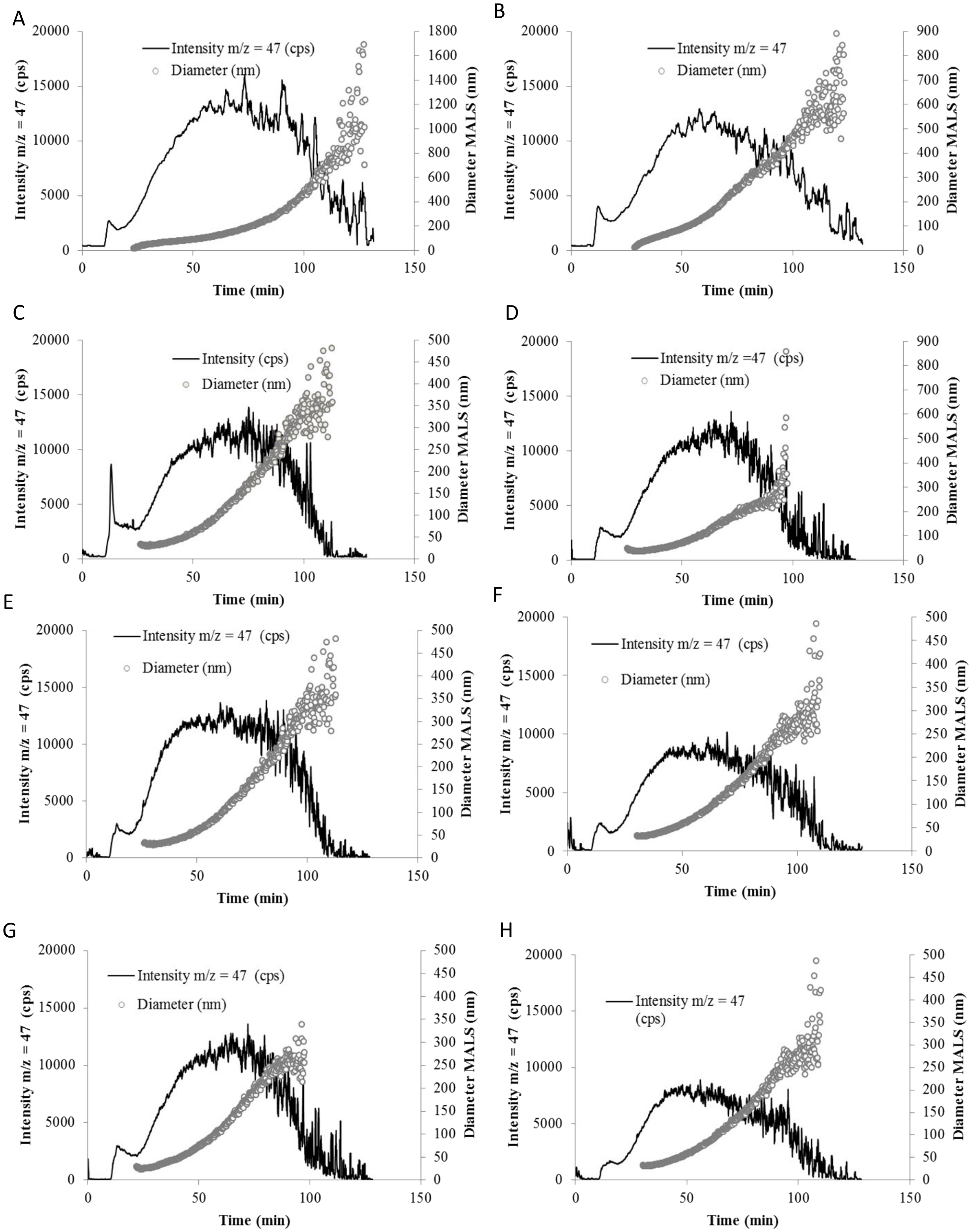
ESI Figure 2 Comparison of the intensity data from the ICP-MS measurement and the size-information obtained based on mathematical calculations using the MALS (dots) signal for the reference material NIST SRM 1898 before (black) and after (grey) the application of the developed sample pretreatment procedure.



ESI Figure 3 Fractograms and size-distribution profiles after spiking and extraction of a natural sediment test sample to compare the effects of different sample preparation procedures (freeze drying vs. direct preparation of the wet fresh sample) including data on the measured gyratic diameter *dg*.



ESI Figure 4 Different fractograms obtained for test mixtures of NIST SRM 2702 spiked with 100 mg/kg NIST SRM 1898 using different extraction solvents (grey cross (water), grey circle (0.05% Tego W752), grey box (0.05% Fl-70))



ESI Figure 5 Compilation of different fractograms showing the particle size-distribution of the investigated lake sediment samples. (A) December 2016 south, (B) December 2016 west, (C) September 2016 south, (D) September 2016 west, (E) June 2016 south, (F) June 2016 west, (G) June 2015 south, (H)June 2015 west.