Commercial titanium dioxide nanoparticles in both natural and synthetic water: comprehensive multidimensional testing and prediction of aggregation behavior

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The Supporting Information consists of 11 pages, 4 tables and 5 figures.

Nanoparticles. The TiO_2 stock dispersions for the matrix testing were prepared by suspending TiO_2 particles (50 mg L^{-1}) in Milli-Q water, followed by 30 minutes of ultrasonication (2×60 W indicated power, Sonorex RK 106 from Bandelin, Germany). The water used (Milli-Q-water) was from a Millipore Advantage A10 system (Millipore, Billerica, US) equipped with a Bio-Pak^{TM} ultrafilter (5000 Dalton molecular weight cut-off) for final clean-up. Suwannee River natural organic matter purchased from the International Humic Substances Society (*8*) was used as an NOM surrogate. The relationship of NOM to dissolved organic carbon (DOC) has been calculated (with a factor of 0.41) and it is therefore used as a synonym for DOC unless otherwise stated. Stock solutions of 10 mM HCl and $NaHCO_3$ were prepared for titration. All reagents were of analytical grade, purchased from Fisher Scientific in Austria. The final TiO_2 concentration in the test vessels prior to the aggregation/settling period was 25 mg L^{-1}.

Water chemistry. Dissolved organic carbon (DOC) was measured using a GE Power & Water DOC analyzer (Sievers 900, USA). The pH and electrical conductivity (EC) were measured using a portable pH/conductivity meter (SenTix 61 and TetraCon 325 probes, respectively: WTW, Germany). Inductively coupled plasma optical emission spectroscopy (ICP-OES) (Optima 5300 DV, Perkin-Elmer, Austria) was used to analyze major cations, i.e. Na^+, K^+, Ca^{2+}, Mg^{2+}, Si^{2+}, Mn^{2+} and Al^{3+}, while Cl^-, NO_3^- and SO_4^{2-} were analyzed by ion chromatography (ICS-1000, Dionex, Austria). The bicarbonate concentration in the natural water was determined by titration to pH 4.3; the HCO_3^- concentration in the EPA water was known from the protocol *(2).*

Nanoparticle analysis. The nanoparticle stability was operationally defined as the fraction of particles in the supernatant after a 15 hour sedimentation time (see also v.d. Kammer et al. 2010). We sampled 10 mL from the supernatant at exactly 2 cm below the surface and determined the pH in the remaining 40 mL. The supernatant was analyzed for nanoparticle concentration, hydrodynamic diameter, and electrophoretic mobility (*1*). In brief, hydrodynamic diameter and electrophoretic mobility were determined by dynamic light scattering (DLS) using a Zetasizer ZS (Malvern Instruments, UK). The method of cumulants was applied to determine the intensity-weighted diffusion coefficient and the hydrodynamic diameter (z-average, 1st cumulant), with each result consisting of ten stacked individual measurements of 10 seconds each. The electrophoretic mobility was measured using laser Doppler anemometry and the zeta potential was calculated from the electrophoretic mobility by applying the Smoluchowski approximation. The isoelectric point (IEP) was determined by running the experiments over a broad pH range. Excluding specific adsorption and assuming H^+/OH^- to be the only potential-determining ions, the isoelectric point equals the point of zero net proton charge and the point of zero charge.

The concentration of TiO_2 in the supernatant was determined by measuring the nephelometric turbidity (Hach 2100N IS Turbiditymeter, LED light source $\lambda = 870$) as described by Battin et al. (*3*). Detection was at 90° angle in a 25 mL glass cell; the correlation between TiO_2 concentration and turbidity is shown in Figure S1. The experiments were carried out in triplicate (n = 3); the results presented show averaged values and the standard deviation (±1SD). Results of the sedimentation tests were plotted on interpolated surface contour plots processed using Surfer 7.0 software (Golden Software, Inc.) with the inverse distance weighting algorithm (Supporting Information).

Table S1. Titanium dioxide characteristics

		Titanium dioxide
	unit	**Aeroxide P25** (4)
CAS-Nr.		13463-67-7
EG-Nr.		236-675-5
TiO_2 content	%	99.9
HCl content	%	0.14
Anatase content	%	88
Rutile content	%	12
Average primary particle size (TEM)	nm	19.8
Particle size (d50) according to ISO 13320	nm	52.2
Specific surface area (BET)	$m\ g^{-2}$	57
Density	$g\ cm^{-3}$	3.8
pH value (40 $g\ L^{-1}$)		3.6
Loss of ignition after drying	w%	1.3
Loss of drying	w%	1.1

Preparation of EPA synthetic test water.

1. Place 4 L Milli-Q-water in plastic carboy
2. Add respective amount of $MgSO_4$, $NaHCO_3$ and KCl (see Table below)
3. Aerate over night
4. Add respective amount of $CaSO_4$ (see Table below) to 1 L Milli-Q-water in a separate flask, stir on magnetic stirrer until calcium sulphate is dissolved, add this to the 4 L
5. Aerate the combined solution vigorously for an additional 24 h to stabilize the medium

Table S2. Reagents used for the preparation of EPA very soft (VS), Moderately hard (MH) and very hard (VH) water

Water type	**Reagent added (mg L^{-1})**				**Approx. water composition**		
	$NaHCO_3$	**$CaSO_4$ $2H_2O$**	**$MgSO_4$ $7H_2O$**	**KCl**	**pH**	**Alkalinity (mg L^{-1})**	**conductivity (µS cm^{-1})**
very soft	12	7.5	15.35	0.5	6.4-6.8	10.0-13	35
moderately hard	96	60	122.86	4	7.4-7.8	57-64	310
very hard	384	240	491.44	16	8.0-8.4	225-245	1046

Auto-titration Protocol. The auto-titration system (Metrohm Titrando 836) was equipped with four individual dosing units (Metrohm Dosino 807) and 20 or 50 mL burettes (Metrohm Dosino 800) and was used together with a robotic sample processor (Robotic sample Processor XL 815) and a fast reaction pH electrode (Metrohm Aquatrode Plus), all devices were purchased from Metrohm, Switzerland. We placed 25 mL of the TiO_2 stock suspension (T_{stock}) in the polyethylene test vessels and then added the electrolyte or NOM stock solution (E/N_{stock}) in respective amount. Preliminary tests revealed the amount of $NaHCO_3$ or HCl needed ($A/B_{estimate}$) to achieve the target pH. To consistently reach a total volume of 50 mL (V_{tot}) in each sample the system calculates the amount of Milli-Q-water (MQ_{final}) needed by the following equation:

$$V_{tot} - T_{stock} - E/N_{stock} - A/B_{estimate} = MQ_{final}$$

Electrode calibration (buffers used were pH 4, 7and 10, Fisher Scientific, Austria) was performed before, after one experimental set, the drift was below ±0.01 pH units. After 15 hours sedimentation 10 mL were sampled with a stainless steel needle in exactly 2 cm depth through a hole in the lid. We analyzed the sample for particle size distribution, concentration and zeta potential. The pH and electric conductivity was measured in the remaining suspension.

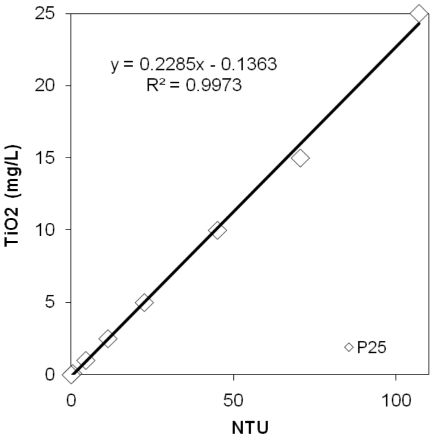

Figure S1. Concentration of TiO_2 P25 versus turbidity.

Interpolation and graphical representation. Results of the sedimentation tests (concentration, particle size and zeta potential) were plotted in interpolated surface contour plots processed by the software Surfer 7.0 (Golden Software, Inc.) with the inverse distance weighting algorithm. The interpolated surface is a distance weighted average of the observed parameters, i.e. with increasing distance between data points their relative contribution to the interpolation declines with distance from the grid node according to equation (1) and (2):

$$Z_j = \frac{\sum_{i=1}^{n} \frac{Z_i}{h_{ij}^{\beta}}}{\sum_{i=1}^{n} \frac{1}{h_{ij}^{\beta}}} \qquad \text{with} \qquad h_{ij} = \sqrt{d_{ij}^2 + \delta^2}$$

where h_{ij} is the effective separation distance between grid node j and the neighboring point i. Z_j is the interpolated value for grid node j; Z_i are the neighboring points; d_{ij} is the distance between the grid node j and the neighboring point i; β is the weighting power and δ is the smoothing parameter determined with 0.

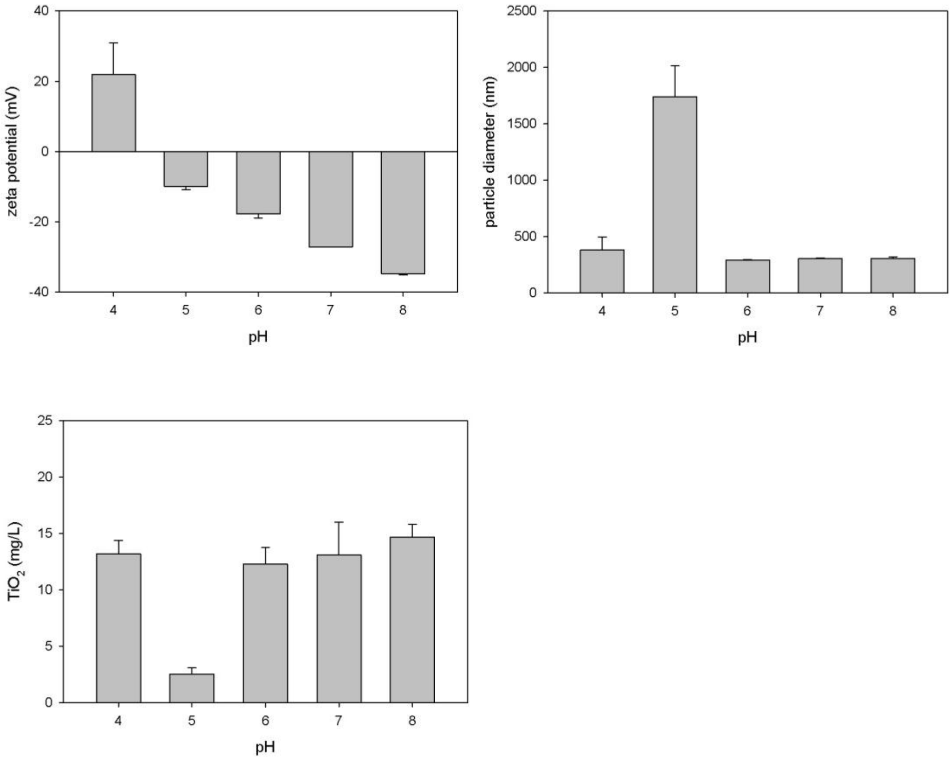

Figure S2. The zeta potential, particle diameter and concentration of TiO_2 nanoparticles in Milli-Q-water titrated to various pH values with 10 mM $NaHCO_3^-$ and 10 mM HCl for pH 4, respectively.

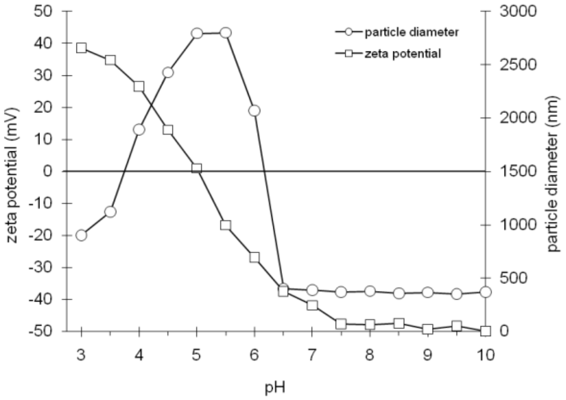

Figure S3. The isoelectric point (IEP) for TiO_2 (25 mg L^{-1}) and respective particle diameter has been determined in Milli-Q-water from pH 3 to 10 (HCO_3^- titration).

Table S3. Examples of compositions of natural waters.

	Rain water (5)	**Lake water** (6)	**River water** (6)	**Seawater** (7)
	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}
Na^+	1.1	0.0	3.1	11145
K^+	0.3	0.0	0.9	414
Mg^{2+}	0.4	6.0	8.7	1339
Ca^{2+}	1.0	45.6	43.0	429
Cl^-	1.1.	2.5	2.8	20065
HCO_3^-	1.2	12.6	9.4	1787
SO_4^{2-}	4.2	15.0	53.0	230

Table S4. Water chemistry of the tested natural water and EPA synthetic water from very soft to very hard (VS, MH, VH). Groundwater from Hoersching (HOE), lake water from Lunz (LUNZ), tap water from a household tap in Vienna (TAP), water from a peat bog at Tanner Moor (TAN), waste water inflow and outflow from a waste water treatment plant (WWTP) in Vienna, (WWI and WWO), all of which are in Austria, and sea water from Normandy, France (FRA).

		Ground water	**Lake water**	**Tap water**	**Peat bog water**	**Sea water**	**Waste water inflow**	**Waste water outflow**	**EPA very soft**	**EPA moderately hard**	**EPA very hard**
	unit	**HOE**	**LUNZ**	**TAP**	**TAN**	**FRA**	**WWI**	**WWO**	**VS**	**MH**	**VH**
EC	µS cm^{-1}	363	246	295	41	56500	1210	1010	35	310	1050
DOC	mg L^{-1}	1.6	2.1	1.0	37.2	<0.5	67.5	10.1	<0.5	<0.5	<0.5
pH		7.8	7.9	8.0	5.2	8.0	8.1	8.2	6.4	7.4	8.4
IS	meq L^{-1}	3.5	1.6	1.8	0.5	146.5	2.9	2.5	0.3	2.5	9.6
HCO_3^-	mg L^{-1}	290	145	161	10	1490	170	120	8	64	255
Na^+	mg L^{-1}	12	n.d.	n.d.	1	8500	37	36	4	32	130
K^+	mg L^{-1}	3	n.d.	n.d.	1	340	18	9	n.d.	2	8
Ca^{2+}	mg L^{-1}	93	46	51	4	430	48	44	2	17	69
Mg^{2+}	mg L^{-1}	20	7	10	n.d.	1300	13	12	2	14	56
Mn^{2+}	mg L^{-1}	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cl^-	mg L^{-1}	18	1	2	7	22500	61	56	n.d.	2	8
NO_3^-	mg L^{-1}	23	4	5	3	n.d.	n.d.	7	n.d.	n.d.	n.d.
SO_4^{2-}	mg L^{-1}	29	2	16	12	2900	45	58	8	41	298
Si^{2+}	mg L^{-1}	4	1	1	5	n.d.	2	2	n.d.	n.d.	n.d.
Al^{3+}	mg L^{-1}	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Fe^{3+}	mg L^{-1}	n.d.	n.d.	n.d.	4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

n.d. = not detectable; all water 0.2 µm filtered

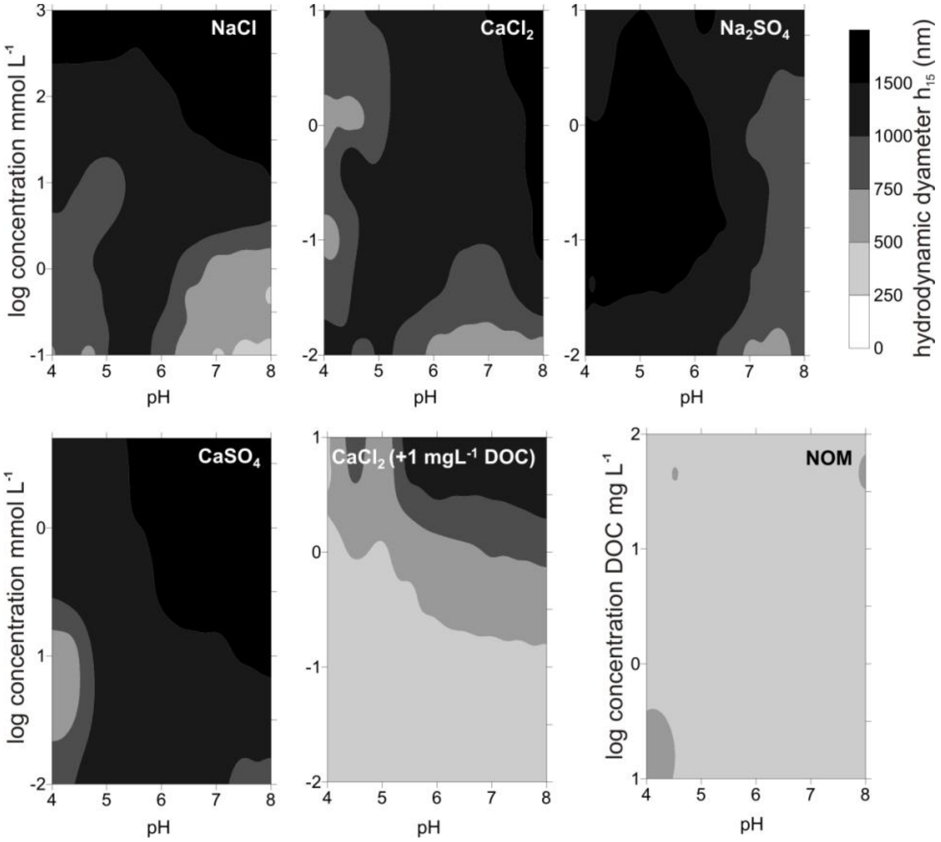

Figure S4. Contour plots of particle stability, expressed as hydrodynamic diameter (nm) in the supernatant after a 15 h aggregation and sedimentation period, as a function of pH and electrolyte concentration or DOC concentration, respectively.

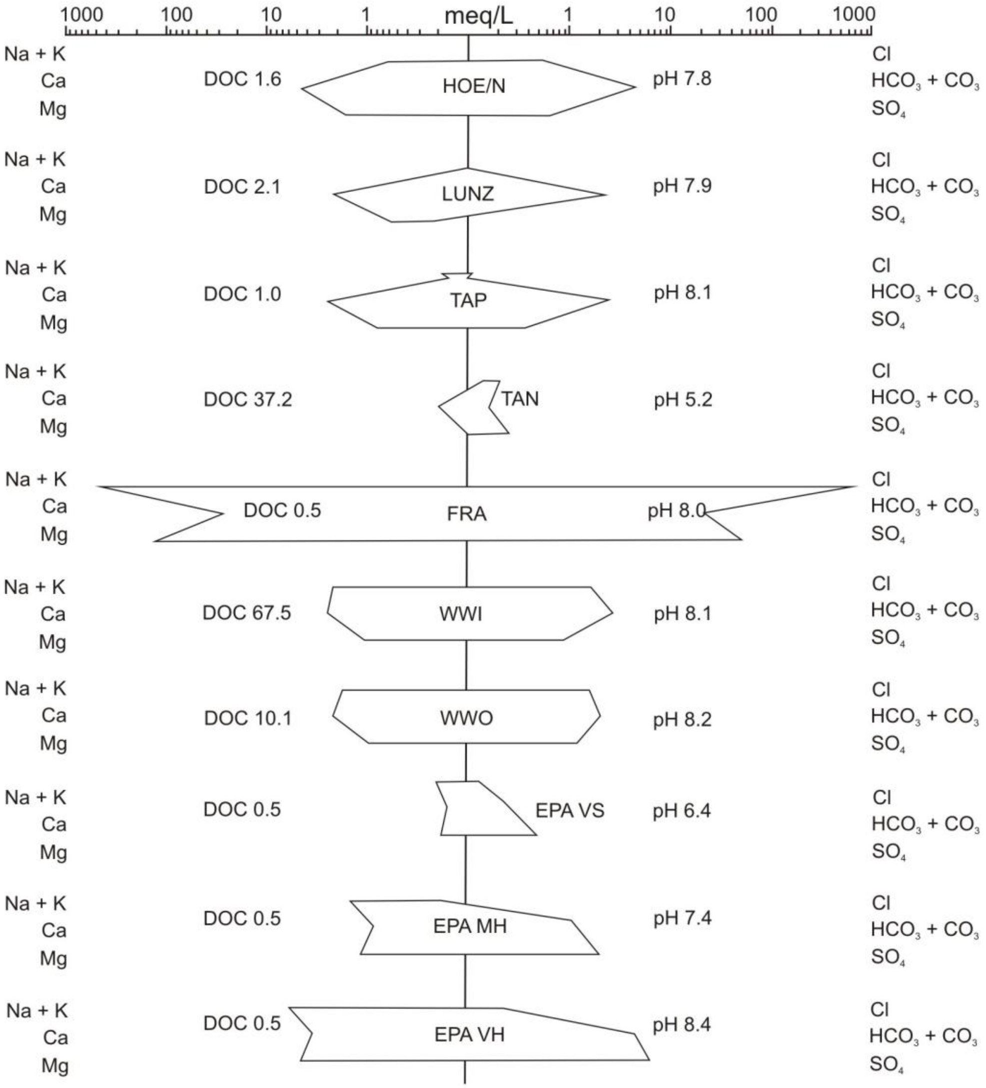

Figure S5. Stiff diagram for a classification of water types on the basis of the water chemistry. The concentration of ions and DOC is in mg L^{-1}.

A Stiff diagram is used to visualize water types and represents the chemical analysis. The Stiff diagram has been developed by H.A. Stiff in 1951. It delivers an easy-to-spot graphical representation of water composition. The cations are plotted in meq/L to the left side of the vertical axis and the anions are plotted to the right side while some of the anions and cations are grouped.

References:

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