

Distribution profile of titanium dioxide nanoparticles in South African aquatic systems


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ABSTRACT

This paper reports the results of a study on the analysis and characterization of titanium dioxide (TiO₂) nanoparticles (NPs) in samples that were collected from selected freshwater dams in South Africa. The study employed a combination of complementary techniques to ascertain the analytical procedures and the occurrence of TiO₂ NPs in water. Characterization, identification and quantification of TiO₂ NPs in surface water samples from five sampled dams was performed using several techniques including scanning electron microscopy-energy dispersive X-ray (SEM-EDX), fluorescence excitation–emission matrix (FEEM) and single particle inductively coupled plasma mass spectroscopy (SP-ICP-MS). The SP-ICP-MS technique was able to simultaneously determine the size and concentration of both the dissolved and particulate titanium (Ti) in water samples. The Ti-containing NPs were found at concentrations ranging from 8.3×10^4 parts/mL to 1.4×10^5 parts/mL in the presence of 14.9 µg/L to 243 µg/L dissolved Ti. The TiO₂ nanoparticles were mostly composed of small agglomerates ranging from 102.9 nm to 158.9 nm in size.

Key words | nanoparticles, SP-ICP-MS, surface water, TiO₂ nanoparticles

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INTRODUCTION

Nanoparticles (NPs) have been reported in various applications, including cosmetics (Aznar *et al.* 2017), biomedicine (Yang *et al.* 2013), food and food packaging (Weir *et al.* 2012), and agriculture and pharmaceuticals (Pestovsky & Martínez-Antonio 2017). Titanium dioxide (TiO₂) NPs are among the most commonly used nanoparticles (Candas-Zapico *et al.* 2018). The significant increase in the application of nanoparticles, particularly TiO₂ NPs, has led to possible risks related to the discharge of engineered nanoparticles (ENPs) in the aquatic environment (Reijnders 2009). When ENPs are released into water systems, some dissolve and pollute the water in addition to accumulating in aquatic organisms, while others get embedded in sediments where they accumulate.

Several studies have reported on the effects of TiO₂ NPs on crustaceans (Heinlaan *et al.* 2008), higher plants (Song

et al. 2013), algae (Hund-Rinke & Simon 2006), and fish (Chen *et al.* 2011) as well as on other aquatic and terrestrial invertebrates (Crane *et al.* 2008). Such effects include the production of oxidative stress, inhibition of Na⁺/K⁺-ATPase, oxidative damage, disturbance of trace elements in tissues, respiratory toxicity in organisms and damaging proteins, carbohydrates and lipids in plants (Yu *et al.* 2011). Moreover, TiO₂ NPs have been reported to cause DNA damage in human intestinal Caco-2 cells (Gerloff *et al.* 2012). However, the toxic impacts of the NPs basically depend on their size, surface properties and concentration (Gerloff *et al.* 2012).

Due to the toxicity of these nanomaterials, many researchers have developed analytical methods for their detection in various water systems. However, in South Africa, very little has been done thus far in relation to the

identification of TiO₂ and other nanomaterials in aquatic systems. Among the few available reports on the occurrence of nanomaterials in South African aquatic environments, is the technical report by Schutte & Focke (2007) which was submitted to the Water Research Commission of South Africa (WRC). In this technical report, there is almost nothing or very little information regarding the occurrence of nanomaterials in South African freshwater systems.

To the best of our knowledge, this is one of the very few scientific studies conducted in South Africa that investigated the occurrence, distribution pattern and fate of nanoparticles (TiO₂) in freshwater systems. The study has developed a novel approach for the simultaneous identification and quantification of NPs, determination of both dissolved and particulate concentrations of TiO₂, size and size distribution of TiO₂ nanoparticles as well as obtaining information regarding agglomeration and aggregation of nanoparticles. The novel method involved the use of a single particle inductively coupled plasma mass spectrometry (SP-ICP-MS). This study will certainly contribute significantly to the knowledge and understanding of the occurrence and fate of nanomaterials in South African freshwater systems.

The aim of this study was therefore to develop and optimize the analytical method for the detection, quantification and characterization of titanium dioxide nanoparticles using SP-ICP-MS and apply the method for the analysis of real environmental freshwater samples.

MATERIALS AND METHODS

Standards and reagents

Gold (Au) NPs suspension (carboxylic acid-capped 50, 100 nm) in pure water was purchased from Perkin Elmer, Johannesburg, South Africa. Gold (1,000 mg/L) and titanium NPs (1,000 mg/L) were purchased from Sigma-Aldrich, Johannesburg, South Africa. DI water (18.2 MΩ cm) was produced using a Milli-Q water purification system (Merck-Millipore S.A.S, France) and Multi-element tune standard solution was purchased from Perkin Elmer, Johannesburg, South Africa.

Water sample collection

Water samples were collected from selected freshwater dams in four South African Provinces, namely Northern Cape (NC), North West (NW), Western Cape (WC), and Free State (FS). The water samples were collected between 19 May and 7 July 2018 from about 10–30 cm depth below the water surface using polypropylene and amber glass bottles with Teflon caps. After sampling, the bottles were placed on ice in a cooler box to protect samples from sunlight and microbial action and were then transported to the laboratory and stored in the dark room at 4 °C prior to analysis. The physico-chemical parameters pH, turbidity, total dissolved solids (TDS) and conductivity (EC) were measured at the sampling site as well as in the laboratory.

STANDARD AND WATER SAMPLE PREPARATION

Water sample preparation

Water samples were filtered using 0.2 μm membrane filters (cellulose acetate) to remove interfering particles prior to scanning electron microscopy-energy dispersive X-ray (SEM-EDX) and SP-ICP-MS analyses. Water samples for fluorescence excitation emission matrices (FEEM) (Aqualog Horiba, Jobin Yvon) were filtered using an Acrodisc[®] Syringe Filter with GHP membrane (0.45 μm, 25 mm).

Standard solution preparation

For size calibration and transport efficiency determination, spherical Au NPs (carboxylic acid-capped 50, 100 nm) in pure water were utilized. Prior to dilution, the Au suspension was sonicated for ten minutes. A few ice cubes were added to the ultrasonic bath to prevent any rise in temperature that might facilitate the dissolution of NPs, as the Au NPs are only stable in the 4–25 °C range according to the certificate provided by the manufacturer (Lamsal *et al.* 2018), and the suspension was diluted in Milli-Q water (18.2 MΩcm). After preparation, the standards were ultrasonicated within five minutes before analysis to ensure that all particles were dispersed (Vidmar *et al.* 2016). Dissolved calibration standards for gold and titanium consisted of 1, 5, and 10 μg/L made

in Milli-Q water from 1,000 mg/L stock standard solutions (Sigma-Aldrich, Johannesburg, South Africa).

The SP-ICP-MS analysis

The analyses were performed on a Perkin Elmer NexION[®] 350D SP-ICP-MS operated in the single particle mode. The instrument was conditioned and optimized as shown in Tables S1 and S2 (Supplementary Material). The 50 and 100 nm Au NP suspensions were used for particle calibration and to determine the transport efficiency. The average flow rate was established by weighing the amount of ultrapure water aspirated in the system for 5 min. Perkin Elmer Syngistix software with Nano Application Module was used for data collection and processing (Bao *et al.* 2016). Prior to the measurement of the water samples, an Au NP (50 nm diameter) was characterized in ultrapure water to confirm the performance of the optimized methodology. The optimized method was applied to the environmental water samples (dam waters). During data acquisition, ultrapure water was analysed between replicates to correct for memory effects (Dan *et al.* 2015; Vidmar *et al.* 2017).

Determination of particle size limit of detection

The size limit of detection (D_{min}) for SP-ICP-MS for nanoparticles was predicted using Equation (1) based on the sensitivity and noise levels in the blank signal (Bi *et al.* 2014; Vidmar *et al.* 2017).

$$D_{min} = \left(\frac{6 \cdot 3\sigma_{DI}}{R \cdot fa \cdot \rho \cdot \pi} \right)^{1/3} \quad (1)$$

where 3σ = the magnitude of the background noise (counts), R = the sensitivity of the detector for the elements in the analyte (counts g^{-1}), which is the slope of the calibration curve that plots the mass entering per dwell (g) in function of the intensity (counts), fa = the mass fraction of the analysed element in the NP and ρ = the density of the NP (19.30 $g\ cm^{-3}$ for Au).

TiO₂ nanoparticle diameter limit of detection (D_{min}) was determined as three times the standard deviation above the background when measuring ultrapure water (blank) by SP-ICP-MS as described previously by Lee *et al.* (2014).

Particle number limit of detection (LOD_{NP})

The nanoparticle number concentration (parts/mL) limit of detection is related to the capability of counting three NP events and can be determined using Equation (2) (Laborda *et al.* 2014; Vidmar *et al.* 2017).

$$LOD_{NP} = 3 * \frac{1}{Q * \eta_{size} * t_s} \quad (2)$$

From Equation (2) it is obvious that nanoparticle number concentration can be attained by improving the transport efficiency (η_{size}), increasing the sample flow rate/sample uptake rate (Q), and/or using longer acquisition times (t_s). The LOD_{NP} for TiO₂ NPs was determined using Equation (2) and was found to be 208 parts/mL (2.08×10^5 parts/L) which is comparable to the NP detection limit of 2.3×10^5 parts/L reported by Vidmar *et al.* (2017).

Limit of detection (LOD) of the dissolved NP

Linear regression analysis was used to determine the LOD for dissolved TiO₂ concentration based on the TiO₂ dissolved calibration curve. It was assumed from the obtained linear calibration curve for dissolved TiO₂ that the SP-ICP-MS response matrix Y was linearly related to the descriptor matrix X for a limited range of concentrations. The limit of detection (LOD) for dissolved TiO₂ was thus determined based on the residual standard deviation of a regression line or the standard deviation (SD) of the y-intercepts of the regression line of the calibration curve and the sensitivity or slope of the regression line, as shown in Equation (3) (Wanda *et al.* 2017).

$$LOD = 3.3 * \frac{SD}{Slope} \quad (3)$$

The LOD for dissolved TiO₂ concentration determined using Equation (3) was found to be 0.27 $\mu g/L$.

SEM-EDX analysis

SEM, JOEL (JSM – IT 300), EDX was used to identify the morphology and the presence of TiO₂ NP in collected

water samples. For SEM/EDX measurements, a drop of the water sample was placed on a glass slide and dried at ambient temperature. Thereafter, the samples were gold-coated prior to SEM/EDX analysis.

FEEM spectroscopy analysis

Fluorescence EEM regional integration method was used to quantify and characterize fluorescent dissolved organic matter (FDOM) as described in previous studies (Chen *et al.* 2003; Zhou *et al.* 2013). Filtered water samples were analysed based on the integration of the total surface and subsequent divisions of the surface into five operationally defined FDOM fractions: tyrosine-like (ex: 220–250 nm; em: 280–330 nm) I, tryptophan-like (ex: 220–250 nm; em: 330–380 nm) II, fulvic acid-like (ex: 220–250 nm; em: 380–550 nm) III, soluble microbial by-product-like (250 nm < ex < 450 nm; em: 280–380 nm) IV, and humic acid-like (250 nm < ex < 450 nm; em: 380–550 nm) V.

Statistical data analysis

Statistical analysis was performed using XLSTAT and SPSS software. The principal component analysis (PCA) and correlation tests were performed using XLSTAT software to determine the association between observations and variables at 95% confidence level. Analysis of variance (ANOVA) was performed using SPSS software to determine variations in the test parameters with respect to between groups and within groups sampling sites at 95% confidence level.

RESULTS AND DISCUSSION

The SP-ICP-MS analysis

Plots of the dissolved and particulate calibration curves for Au dissolved fraction, Au particle fraction and TiO₂ dissolved fraction showed good linearity with correlation coefficients (r^2) of 0.99994, 0.99981, and 0.99828 for Figure 1(a)–1(c), respectively. The resulting mean size distribution of Au NPs was found to be 51 nm (Figure 2), which corresponded to the certificate value supplied by

the manufacturer. The results obtained from the analysis of water samples are presented in Table 1. Except for particle concentration, the rest of the parameters (most frequent size, mean size, and dissolved concentration) registered statistically significant variations with respect to sampling sites, p -value < 0.05 at 95% confidence level (Table 2).

SEM-EDX analysis

Figure 3 shows the SEM micrograph and the EDX spectrum of the water sample from NW Dam. The EDX analysis of the water sample identified silica (Si), carbon (C), aluminium (Al), calcium (Ca), magnesium (Mg), sodium (Na) and titanium (Ti) with the decrease in percentage weight respectively. The EDX results tentatively identified the existence of Ti particles, although in trace amounts which suggest the presence of TiO₂ nanoparticles (Tulve *et al.* 2015). However, the presence of Ti containing nanoparticles in water samples was identified beyond reasonable doubt and confirmed by the SP-ICP-MS as shown in Table 1.

Influence of environmental variables on the occurrence of TiO₂ nanoparticles

The environmental variables, such as pH, EC, turbidity, TDS and dissolved organic matter (DOM), tend to have an influence on the properties of NPs, and may determine their persistence, bioavailability, transport and potential toxicity to exposed organisms (Li *et al.* 2010). In all of the sampled dams, the possible sources and levels of TiO₂ NPs may be attributed to natural processes (Bystrzejewska-Piotrowska *et al.* 2009) as well as human activities such as agricultural activities that take place round the dams. Moreover, as has been reported, products containing NPs that are intended for agricultural usage (Kah *et al.* 2013; Peters *et al.* 2016; Pestovsky & Martínez-Antonio 2017) have already been introduced to the market and the application of such products by farmers around these dams might have acted as sources for their occurrence in the dam waters. Most of these dams were constructed to cater mainly for agricultural activities. In addition, recreational activities and the use of products containing NPs such as textiles, cosmetics, fabrics and plastics may eventually release nanomaterials into the

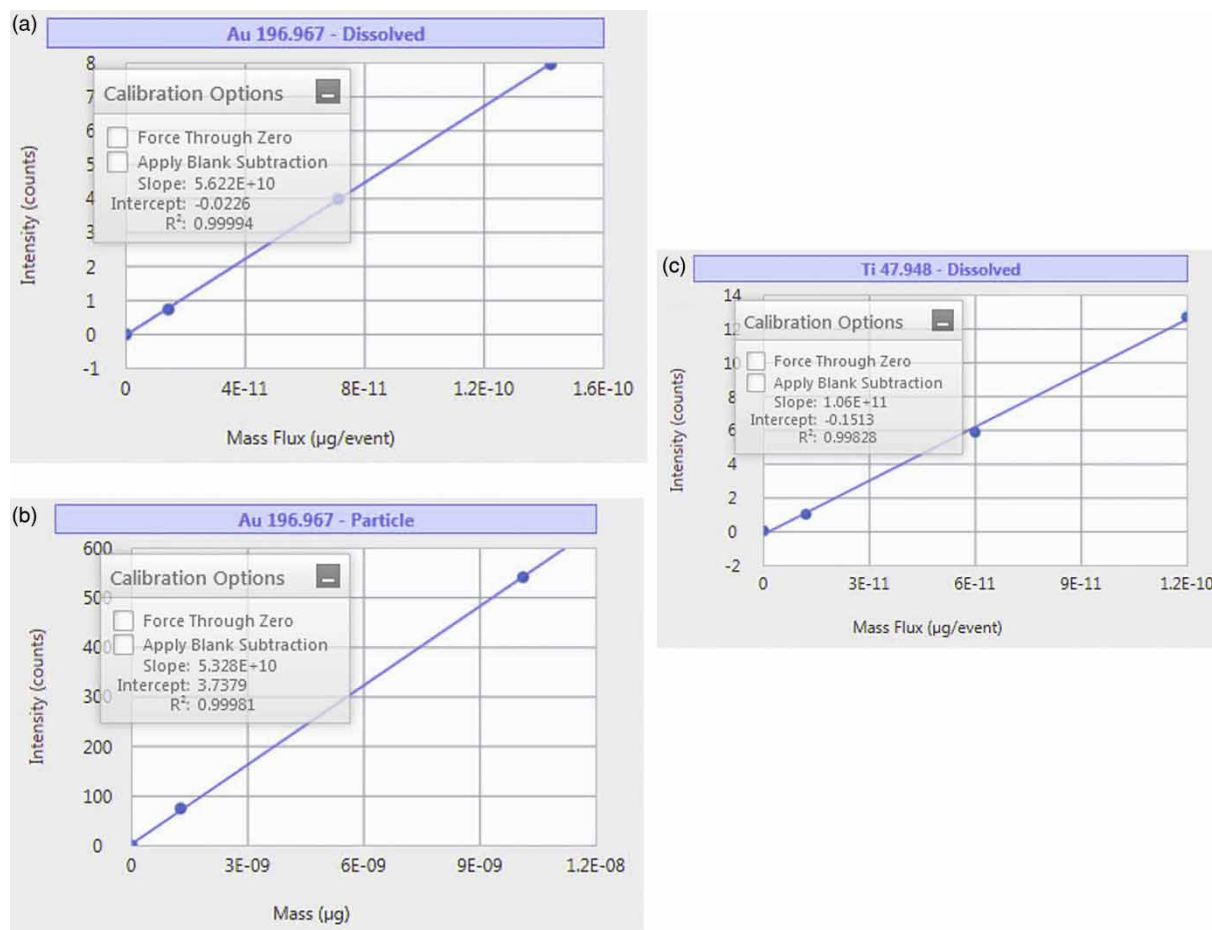


Figure 1 | Calibration standard curves for Au dissolved fraction (a), Au particle fraction (b) and TiO_2 dissolved fraction (c).

water thus posing a potential exposure risk to the aquatic environment (Pestovsky & Martínez-Antonio 2017).

In this work therefore, samples collected from several dams were analysed for the presence of nanomaterials and the relationship between the environmental variables and the presence of TiO_2 NPs in the respective dams was investigated. The descriptive statistics for all the investigated parameters are given in Table 3. However, for better visualization of the descriptive statistics, a standardization technique (a rescaling from 0 to 1) was carried out and is presented in Figure 4.

Table 4 represents the principal components (PCs) generated by the PCA model. The first two PCs accounted for 82.720% of the total variation in the data. Principal Component 1 (PC1) accounted for 63.727% of the variation in the original dataset for water samples from the study area.

Principal Component 2 (PC2) accounted for 18.993% of the variation in the original dataset. This indicates that more than 80% of the total variation can be accounted for with the first two PCs or axes.

Moreover, the results in Table 4 show that PC1 registered strongly positive correlations in TDS and EC, mean size, dissolved concentrations, most frequent size, tyrosine-like, tryptophan-like, microbial by-product-like fractions and negative correlations in fulvic acid-like and humic acid-like fractions. This suggests that all the above-mentioned variables with positive correlations have a similar influence on the occurrence of TiO_2 NPs and they are unaffected by fulvic acid-like and humic acid-like fractions. This also suggests that these eight positively correlated variables vary together. Table 4 also shows PC1 correlates more strongly with mean size. In fact, we could state that based on the

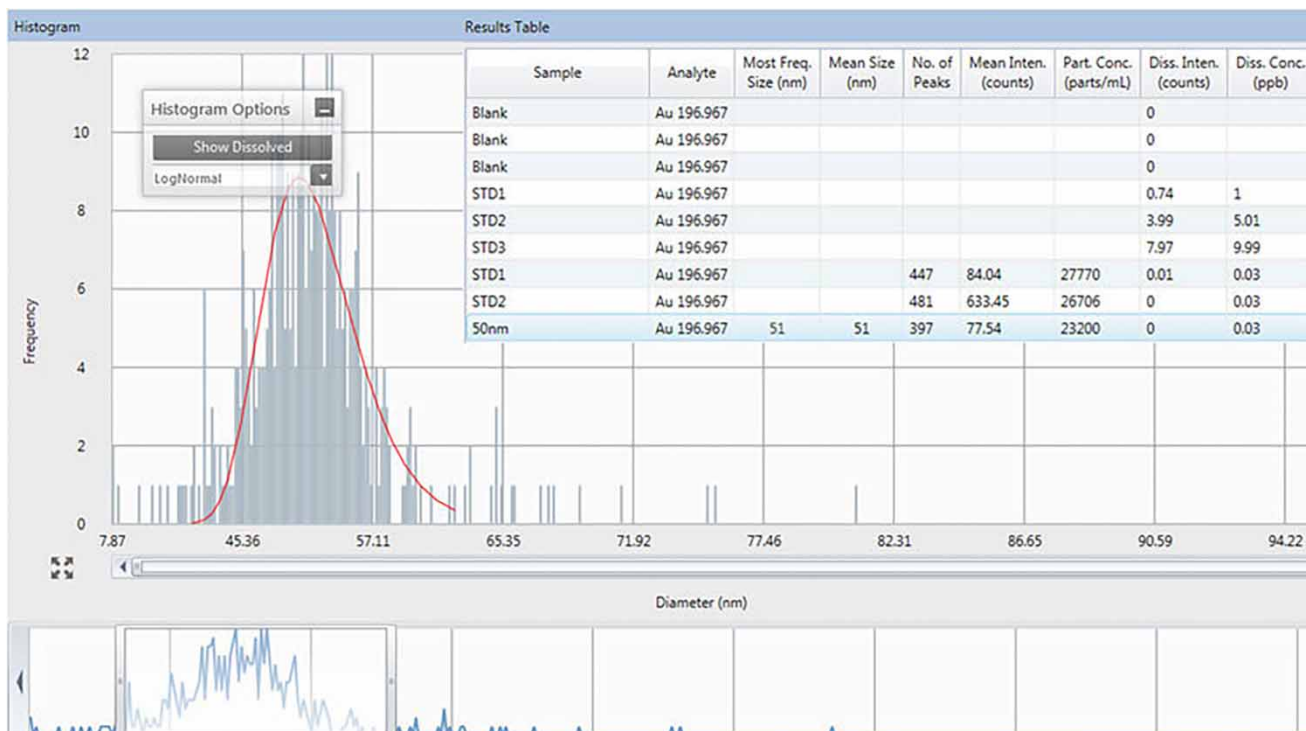


Figure 2 | Size distribution histogram of 50 nm Au prepared in ultrapure water from Syngistix Nano Application Module for SP-ICP-MS. Inset shows the table of results.

Table 1 | Mean value of size, concentration of dissolved and particulate Ti (naturally or engineered nanomaterials) in water samples from five dams

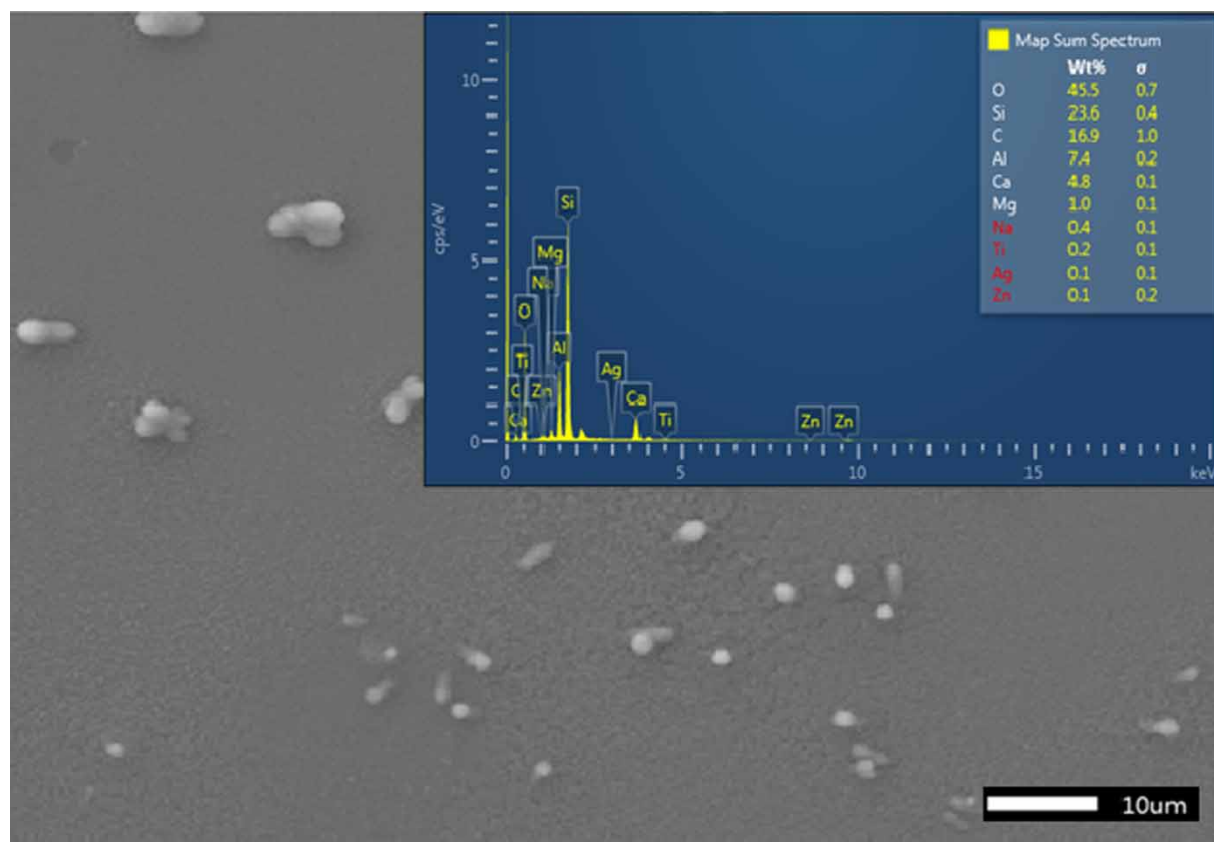
Sampling site	Most freq. size (nm)	Mean size (nm)	Part. conc. (parts/mL)	Dissolved conc. ($\mu\text{g/L}$)
NW Dam	158.92	168.04	1.23E+05	243.94
WC1 Dam	102.91	118.68	1.30E+05	15.19
FS Dam	124.85	131.65	8.77E+04	93.91
WC2 Dam	103.16	118.81	1.38E+05	14.87
NC Dam	136.41	141.90	8.31E+04	131.41

correlation value of 0.905, this principal component is primarily a measure of the mean size. This also suggests that the mean size increases with increasing TDS, EC, dissolved concentration, and tyrosine-like, tryptophan-like and microbial by-product-like fractions. On the other hand, PC2 registered positive correlations with particle concentration and pH and negative correlation with turbidity. It also suggests that both particle concentration and pH might have had a similar influence on the occurrence of TiO_2 NPs, which are weakly affected by the turbidity. Furthermore, the PC2 (correlation of 0.699) could be primarily considered as a measure of the particle concentration.

The correlations between investigated variables are summarized in Table 5 and Figure 5. The values in bold (in Table 5) indicate that they are statistically significant at a 95% confidence interval. The observation indicates that there is a strong positive correlation between mean size, TDS, conductivity, most frequent size and the tryptophan-like fraction which suggests that the mean size of the TiO_2 NPs in dam water increases with the increase in total dissolved solids, conductivity, dissolved concentrations and natural organic matter (tryptophan-like). It was also observed that, as the conductivity (as an indicator of ionic strength) increased, it allowed for more particle-particle interactions resulting in an increase in the hydrodynamic sizes of the particles which is also in agreement with previous findings (Batley *et al.* 2012). However, the presence of FDOM may likely lead to the increase in size as well as stability of the nanoparticles due to the adsorption of FDOM (tryptophan-like) on the surface of nanoparticles thus forming a surface coating which increases the average thickness of the NPs. In addition, the interactions between FDOM and nanoparticles may determine the persistence and

Table 2 | Analysis of variance (ANOVA)

		Sum of squares	df	Mean square	F	Sig.
Most frequent size	Between groups	6,113.565	4	1,528.391	1,036.005	0.000
	Within groups	10.327	7	1.475		
	Total	6,123.892	11			
Mean size	Between groups	4,665.252	4	1,166.313	209.761	0.000
	Within groups	38.921	7	5.56		
	Total	4,704.173	11			
Particle concentration	Between groups	5,513,132,780	4	1,378,283,195	1.028	0.455
	Within groups	9,386,683,940	7	1,340,954,849		
	Total	14,899,816,721	11			
Dissolved concentration	Between groups	99,999.33	4	24,999.832	7,424.401	0.000
	Within groups	23.571	7	3.367		
	Total	100,022.9	11			

**Figure 3** | SEM micrograph of water sample from NW Dam. Inset shows the EDX spectrum results.

bioavailability of TiO_2 nanoparticles and their potential toxicity to biological systems in case of exposure. Furthermore, the increase in mean size also correlated positively

with dissolved concentrations and TDS, presumably due to more particles being available for interaction (Hadioui *et al.* 2014, 2015).

Table 3 | Descriptive statistics for all the environmental variables investigated

Statistic	Most freq. size (nm)	Mean size (nm)	Part. conc. (parts/mL)	Dissolved conc. ($\mu\text{g/L}$)	pH	Conductivity ($\mu\text{S/cm}$)	Turbidity (NTU)	TDS (ppm)	Tyrosine- like (Intensity, RU)	Tryptophan- like (Intensity, RU)	Fulvic acid-like (Intensity, RU)	Microbial by- product- like (Intensity, RU)	Humic acid-like (Intensity, RU)
No. of observations	5	5	5	5	5	5	5	5	5	5	5	5	5
Minimum	102.910	118.677	83,117.970	14.870	7.450	42.200	5.800	20.700	0.021	0.031	0.176	0.054	0.528
Maximum	158.923	168.043	138,401.900	243.940	8.700	540.667	158.700	268.100	0.068	0.086	0.191	0.154	0.704
Range	56.013	49.367	55,283.930	229.070	1.250	498.467	152.900	247.400	0.047	0.055	0.015	0.100	0.176
1st Quartile	103.160	118.810	87,692.955	15.187	7.533	50.533	32.667	20.700	0.040	0.053	0.176	0.110	0.552
Median	124.845	131.650	123,186.890	93.905	8.100	131.650	43.400	25.033	0.062	0.053	0.177	0.137	0.567
3rd Quartile	136.410	141.900	130,194.873	131.405	8.367	150.500	66.400	76.000	0.065	0.055	0.189	0.143	0.609
Mean	125.250	135.816	112,518.918	99.861	8.030	183.110	61.393	82.107	0.051	0.056	0.182	0.119	0.592
Variance (n)	449.129	335.186	515,383,592.585	7,236.494	0.230	33,798.103	2,746.651	9,085.947	0.000	0.000	0.000	0.001	0.004
Variance (n-1)	561.412	418.983	644,229,490.732	9,045.617	0.288	42,247.629	3,433.314	11,357.434	0.000	0.000	0.000	0.002	0.005
Standard deviation (n)	21.193	18.308	22,702.061	85.068	0.480	183.843	52.408	95.320	0.018	0.018	0.007	0.036	0.062
Standard deviation (n-1)	23.694	20.469	25,381.676	95.108	0.536	205.542	58.594	106.571	0.020	0.020	0.007	0.040	0.069
Variation coefficient	0.169	0.135	0.202	0.852	0.060	1.004	0.854	1.161	0.356	0.314	0.036	0.300	0.104

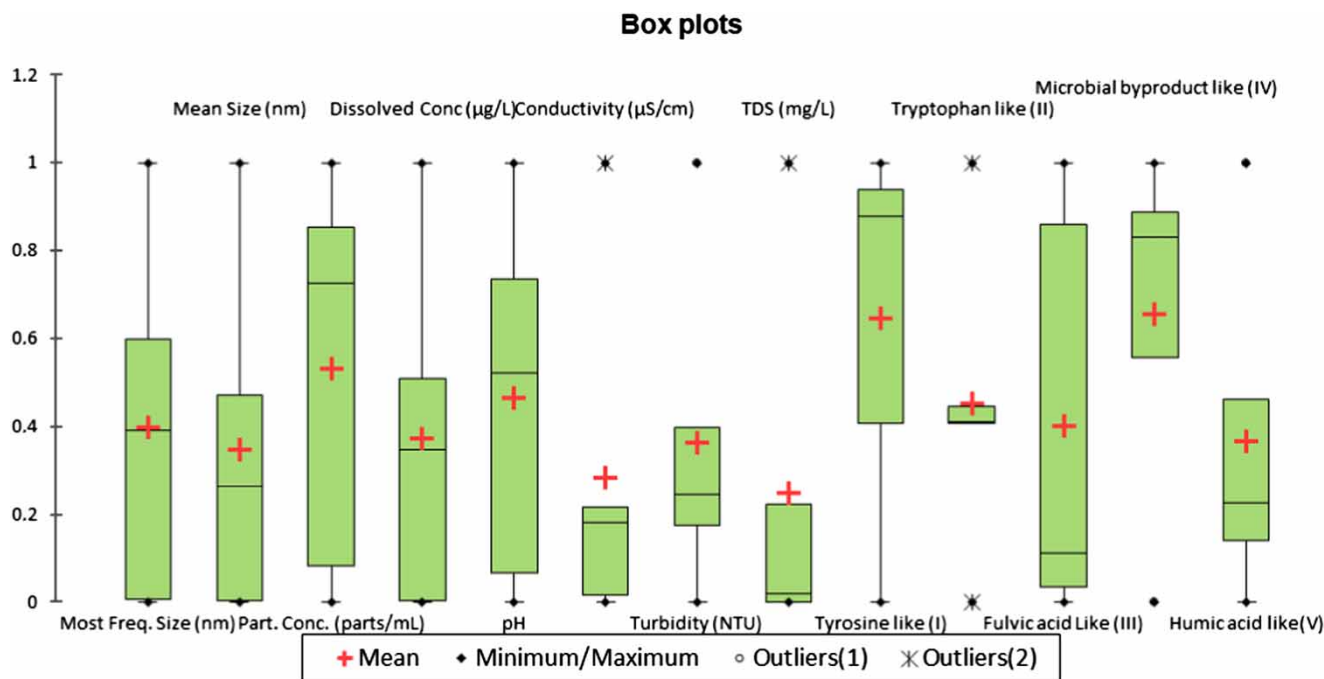


Figure 4 | Box plots showing investigated parameters; conductivity ($\mu\text{S}/\text{cm}$), mean size (nm), dissolved concentrations ($\mu\text{g}/\text{L}$), most frequent size (nm), particle concentration (parts/mL), turbidity (NTU), pH, TDS (mg/L) and dissolved organic matter (Tyrosine-like, Tryptophan-like, Fulvic acid-like, Soluble microbial by-product-like and Humic acid-like) Intensity (RU).

Table 4 | Correlations between variables and factors extracted using the PCA

Variable	Principal Component 1	Principal Component 2
Most freq. size (nm)	0.88	-0.464
Mean size (nm)	0.905	-0.375
Part. conc. (parts/mL)	-0.09	0.699
Dissolved conc. ($\mu\text{g}/\text{L}$)	0.888	-0.437
pH	0.616	0.782
Conductivity ($\mu\text{S}/\text{cm}$)	0.862	-0.299
Turbidity (NTU)	-0.373	-0.538
TDS (mg/L)	0.876	-0.166
Tyrosine-like (Intensity, RU)	0.859	0.381
Tryptophan-like (Intensity, RU)	0.962	-0.091
Fulvic acid-like (Intensity, RU)	-0.845	-0.446
Microbial by-product-like (Intensity, RU)	0.813	0.199
Humic acid-like (Intensity, RU)	-0.908	-0.155
Variability (%)	63.727	18.993
Cumulative %	63.727	82.720

Figure 6 presents the association between active variables and active observations (sampling areas) of the

extracted principal components. The results show that the occurrence of the TiO_2 NPs in water samples collected from different dams in South Africa is influenced by the physicochemical water quality parameters loaded in a particular principal component. The water samples collected from NW Dam seem to be significantly influenced by the parameters highly loaded in PC 1 (F1) and moderately influenced by the parameters highly loaded in PC 2 (F2). The water samples from WC1 Dam seem to be virtually unaffected by the parameters highly loaded in PC1 (F1) and moderately influenced by the parameters highly loaded in PC2 (F2). The water samples from FS Dam seem to be virtually unaffected by the parameters highly loaded in both PC1 (F1) and PC2 (F2). The water samples from WC2 Dam seem to be moderately influenced by the parameters highly loaded in PC1 (F1) and significantly influenced by the parameters highly loaded in PC2 (F2). The water samples from NC Dam seem to be significantly influenced by the parameters highly loaded in PC1 (F1) and moderately influenced by the parameters highly loaded in PC2 (F2).

Table 5 | Correlation matrix (Pearson) for the investigated variables

Variables	Most freq. size (nm)	Mean size (nm)	Part. conc. (parts/mL)	Dissolved conc. ($\mu\text{g/L}$)	pH	Conductivity (μS)	Turbidity (NTU)	TDS (ppm)	Tyrosine- like (I)	Tryptophan- like (II)	Fulvic acid-like (III)	Microbial by-product- like (IV)	Humic acid- like (V)
Most freq. size (nm)	1	0.986	-0.385	0.996	0.170	0.912	-0.147	0.876	0.554	0.872	-0.537	0.592	-0.697
Mean size (nm)	0.986	1	-0.228	0.996	0.246	0.963	-0.285	0.944	0.566	0.901	-0.562	0.557	-0.686
Part. conc. (parts/mL)	-0.385	-0.228	1	-0.304	0.450	0.003	-0.694	0.101	-0.021	-0.054	-0.035	-0.301	0.200
Dissolved conc. ($\mu\text{g/L}$)	0.996	0.996	-0.304	1	0.193	0.946	-0.201	0.913	0.548	0.892	-0.531	0.562	-0.684
pH	0.170	0.246	0.450	0.193	1	0.271	-0.578	0.372	0.858	0.531	-0.879	0.700	-0.716
Conductivity (μS)	0.912	0.963	0.003	0.946	0.271	1	-0.388	0.982	0.498	0.902	-0.484	0.423	-0.597
Turbidity (NTU)	-0.147	-0.285	-0.694	-0.201	-0.578	-0.388	1	-0.545	-0.283	-0.254	0.464	-0.054	0.138
TDS (ppm)	0.876	0.944	0.101	0.913	0.372	0.982	-0.545	1	0.535	0.877	-0.563	0.433	-0.598
Tyrosine-like (I)	0.554	0.566	-0.021	0.548	0.858	0.498	-0.283	0.535	1	0.788	-0.965	0.958	-0.971
Tryptophan-like (II)	0.872	0.901	-0.054	0.892	0.531	0.902	-0.254	0.877	0.788	1	-0.716	0.733	-0.865
Fulvic acid-like (III)	-0.537	-0.562	-0.035	-0.531	-0.879	-0.484	0.464	-0.563	-0.965	-0.716	1	-0.907	0.908
Microbial by-product-like (IV)	0.592	0.557	-0.301	0.562	0.700	0.423	-0.054	0.433	0.958	0.733	-0.907	1	-0.974
Humic acid-like (V)	-0.697	-0.686	0.200	-0.684	-0.716	-0.597	0.138	-0.598	-0.971	-0.865	0.908	-0.974	1

Values in bold are different from 0 with a significance level $\alpha = 0.05$.

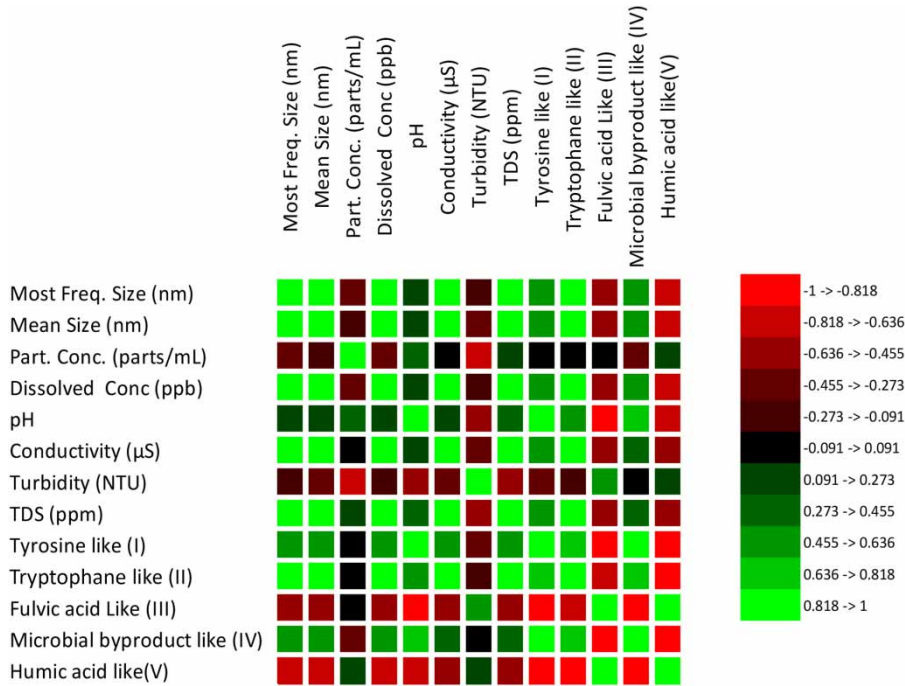


Figure 5 | Heat maps for the correlation matrix.

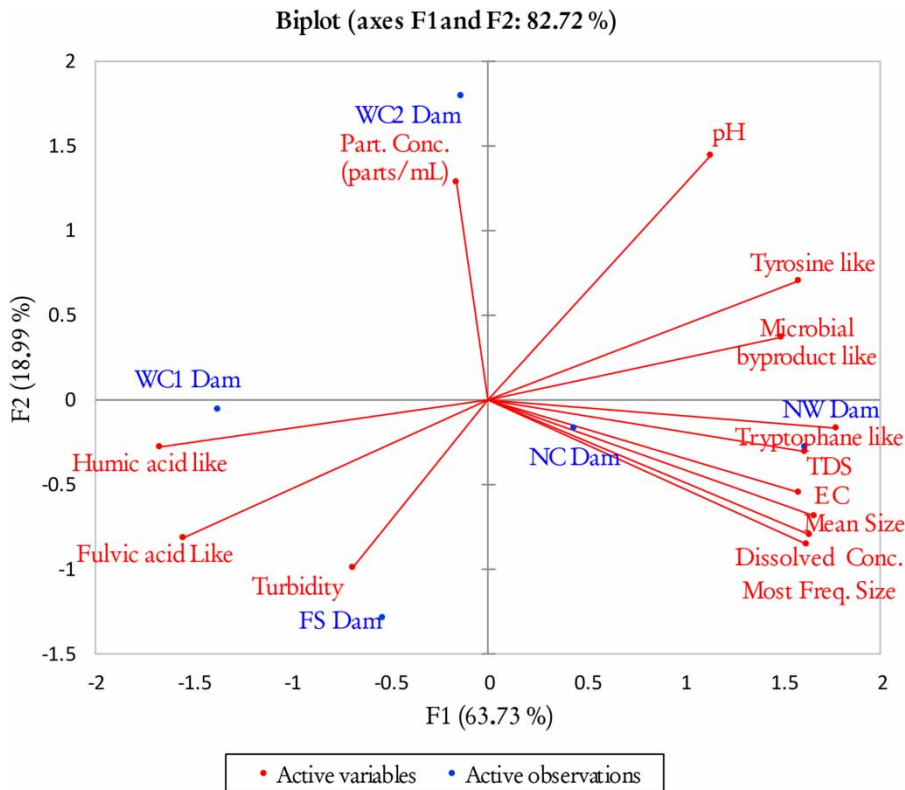


Figure 6 | Biplot showing correlation between variables and observations (sampling areas).

CONCLUSION

In this study, both confirmatory and complementary techniques were employed for the analysis and characterization of TiO₂ NPs in water from selected dams in South Africa. The results have indicated the presence of TiO₂ NPs in the water samples from the five selected dams. The mean size of detected TiO₂ nanoparticles was found to range from 102.9 nm to 158.9 nm, while the mean nanoparticle number concentration ranged from 8.3×10^4 parts/mL to 1.4×10^5 parts/mL in the presence of 14.9–243 µg/L dissolved Ti concentration. The magnitude in terms of mean size, nanoparticle number concentration and dissolved concentration of the Ti containing nanoparticles from the various dams, was found to be influenced by water chemistry (physicochemical properties) and hydrogeochemical properties. The use of the SP-ICP-MS technique has proved to be valuable with respect to the determination of size and concentration of the TiO₂ nanoparticles in the aquatic environment.

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SUPPLEMENTARY MATERIAL

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