Aggregation and deposition of engineered TiO\textsubscript{2} nanoparticles in natural fresh and brackish waters

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Abstract. The use and thus environmental release potential of metal-based nanoparticles have rapidly increased. Due to their size-dependent new properties, the fate and effect of nanomaterial may differ from those of the conventional form of corresponding material. The agglomeration and sedimentation were studied by spiking the TiO\textsubscript{2}-P25 particles in natural fresh and brackish water samples. The natural waters were determined for conductivity, pH, salinity, total organic carbon, turbidity, common nutrients and trace elements. The hydrodynamic diameter and concentration of TiO\textsubscript{2}-P25 particle dispersions were monitored by using a dynamic light scattering and a spectrophotometer, respectively. The experiments were performed at two particle concentrations 100 mg/l and 1 mg/l (10 mg/l for deposition studies). The aggregation rates in brackish waters were clearly higher in higher initial concentration and the sedimentation of aggregates decreased the TiO\textsubscript{2} concentration down to 20% and 80% of initial higher and lower concentrations, respectively. One fresh water sample favoured the destabilisation of TiO\textsubscript{2}-P25 particles whereas another fresh water sample stabilised the TiO\textsubscript{2} particle dispersion. The aggregation had a strong dependence on the particle concentration. High ionic content of brackish water probably explains the formation of aggregates, whereas organic substances and pH may account for the different agglomeration behaviour in fresh waters.

1. Introduction

Nanosized materials have attracted the science community due to their unique physicochemical properties. These materials have been used in various scientific fields including engineering, biotechnology, biomedical, environmental and materials sciences. This has resulted in a number of new technical innovations and applications. Currently, there are hundreds of consumer products containing nanomaterials in global markets [1-2] and the number is increasing annually. Due to new properties associated with conventional or surface modified materials at nanoscale, some of nanomaterials may have exceptional environmental behavior and effects. The products containing nanomaterials can be divided in three groups on a basis of the location of nanomaterials: nanomaterials in bulk (e.g. composite materials), nanomaterials on the surface (e.g. textiles, catalysts, sun energy cells) and nanomaterials in dispersion (e.g. paints, sprays, cosmetics) [3]. The last two of the groups are expected to have potential to release nanomaterials to environment during the use of products.

Due to the commercial relevance, high production and potential adverse effects, engineered TiO\textsubscript{2} nanomaterials have been chosen as one of fifteen nanomaterials for extensive testing program.
coordinated by the OECD Working Group of Manufactured Nanomaterials [4]. TiO$_2$ nanoparticles have already been utilized in numerous applications. They have been widely used in sun creams to improve the UV blocking. In addition, TiO$_2$ nanoparticles have mixed as a dye into paints and attached as photocatalysts onto the different surfaces. Kaegi et al. [5] reported the release TiO$_2$ particles from the facade paints by natural weather conditions. They measured the concentration of TiO$_2$ in runoff water to be 13.4 µg/l and a part of this appeared at a nanoscale. Based on the modeling study of ENP emissions in Switzerland, the predicted environmental concentration (PEC) of engineered TiO$_2$ nanomaterials is 16 µg/l in surface waters [6].

There are a number of studies dealing with the aggregation and deposition of engineered nanoparticles [e.g. 7-12]. These studies have been conducted nearly without exception under the controlled test condition by adjusting the pH, ionic strength, composition of mono- and divalent ions as well as the concentration of dissolved organic matter. However, while providing valuable knowledge, particle behavior in model laboratory systems might not be representative of that observed in far more complex natural environments. This paper focuses on the aggregation and transport potential of engineered TiO$_2$ particles in four different natural waters. The differences in particle behavior observed during the experiments are compared with the physicochemical water quality characteristics of tested natural waters. All the experiments have been conducted at two initial concentrations of nanoparticles. To our best knowledge, this is the first paper that focuses on the behavior and fate of engineered TiO$_2$ particles in natural waters typical to Nordic conditions.

2. Materials and Methods

2.1. Nanomaterial and preparation of dispersion
Titanium dioxide nanoparticles (TiO$_2$-P25; Evonik Degussa GmbH, Germany) were purchased as a white powder with a nominal primary diameter of 21 nm. Figure 1 shows the image of the TiO$_2$-P25 powder by using a Field Emission Scanning Electron Microscopy (see section 2.3.4.). Stock dispersions were prepared by adding 100 mg of TiO$_2$-P25 powder into 100 ml of deionised Milli-Q water. Test samples were prepared by spiking a 30-min sonicated stock dispersion in test matrix at a ratio of 1:9. The particle size was measured prior to each experiments.

2.2. Natural water samples
The agglomeration and deposition of engineered TiO$_2$ nanoparticles were studied in two different fresh and brackish waters. The natural waters were sampled at a depth of 1 meter between May 18 and 20, 2010. The samples were stored at 4°C under dark conditions until needed. The sampling sites are described briefly below.

Simijärvi (60°10 N, 23°33 E). Simijärvi is located at a village of Antskog about 75 km west of Helsinki. It represents a unique lake of esker area that is characterized by clear water and the scarcity of aquatic vegetation. Simijärvi is mainly surrounded by rocky coniferous forest. The water sample was collected on May 19, 2010.

Iso Lehmälampi (60°21 N, 24°36 E). Iso Lehmälampi (60°21 N, 24°36 E) is a small lake (0.03 km$^2$) that is situated on an upland area about 25 km from the southern coast of Finland. The lake itself consists of two parts; the shallower north-western part and the deeper south-eastern part. Due to the hilly topography of the area, which is characterized by bedrock outcrops, the drainage area is very small. The modern forest around the lake is composed of Scots pines, Norway spruces, birches and Alder trees. Iso Lehmälampi water was sampled on May 20, 2010. The surroundings of the sampling site have been described in detail elsewhere [13].

Tvärminne (59°50 N, 23°15 E). The Tvärminne Zoological Station (University of Helsinki) is located on a shore of western Gulf of Finland at Hanko, the southmost town in Finland. The Tvärminne area is not directly affected by large sewage outlets, but nutrients are unintentionally, but frequently introduced to the productive surface layer. The Tvärminne sample was collected at
Zoological Station about 10 meters from the coastline. Coastal seawater was sampled on May 18, 2010.

Lånskär (59°82'N, 23°28'E). Långskär is the southernmost island of outer archipelago of Hanko area. The sample was collected on open sea zone 2 km south of Långskär. The Gulf of Finland is the easternmost part of the Baltic Sea. Its salinity at the surface is typically clearly below 10‰. Open and coastal seawaters were sampled at the same day (May 18, 2010). The surroundings of the sampling site have been described in detail Elsewhere [14].

The water samples were filtered (cellulose acetate membrane filter, pore size 0.45 µm, Whatman, Germany) to remove the large colloidal particles that may interrupt the measurements. The agglomeration of engineered TiO₂ nanoparticles were studied by spiking nanoparticle suspension in natural water samples at concentration of 1 mg/l and 100 mg/l. Due to the detection limit of spectrophotometer, the deposition studies were done at the concentrations of 10 mg/l and 100 mg/l. The measurements were started immediately after each spiking and all the experiments were done in duplicate samples.

2.3. Analytical instruments

2.3.1. Characterisation of natural water samples. All analyses were carried out at the SYKE Environment Measurement and Testing Laboratory, which is accredited as a testing laboratory (T003) by the Finnish Accreditation Services, FINAS (SFS-EN ISO/IEC 17025). Natural waters were analysed by using the analytical instruments as follows: a 815 Robotic USB Sample Processor XL (Metrohm Ion analysis, Switzerland) for conductivity, a 814 USB Sample Processor (Metrohm Ion analysis, Switzerland) for pH, a Salinometer Autosal 8400B (Guildline Instruments Ltd, UK) for salinity, a titrator (Titrator Mettler DL70Es, Mettler Toledo, USA) for alkalinity, a Total Organic Carbon Analyzer (TOC-V CPH/CPN; Shimadzu, Japan) for total inorganic carbon (TIC) and total organic carbon (TOC), a turbidimeter (HACH 2100 AN IS, Hach company, USA) for turbidity, a continuous flow analyser (BRAN+LUEBBE AutoAnalyzer3, BRAN+LUEBBE, Germany) for silicon dioxide and nitrogen, a comparator (Hellige Neo comparator, Nessler, Germany) for water colour, an ion chromatography (Dionex DX500, Dionex corporation, USA) for chloride, fluoride and sulphate and a spectrophotometer (Hitachi U-2000, Japan) for phosphorus. The chemical oxygen demand (COD₅₅) and dissolved oxygen were determined with titrimetric method by following the Finnish standards SFS3036 and SFS3040, respectively. The trace elements were analysed by using either an inductively coupled plasma optical emission spectrometry (ICP-OES; Varian Vista PRO Radial, Varian Incorporation, USA) or an inductively coupled plasma mass spectrometry (ICP-MS; Perkin Elmer ELAN 6000, Perkin Elmer corporation, USA).

2.3.2. Dynamic Light Scattering. A dynamic light scattering (DLS; Malvern Zetasizer Nano S, model ZEN 1600, Malvern Instruments, United Kingdom) was used to monitor the hydrodynamic diameter of TiO₂-P25 particles spiked in different natural waters. The increase of particle size indicates the formation of aggregates or agglomerates (hereafter only the term aggregates is used in the text). The DLS was operated with a He-Ne laser at a wavelength of 633 nm and light scattering was detected at an angle of 173°. Prior to analysis, 1 ml of sample added in polystyrene cuvette was stabilised at 25°C. The data presented in this paper are based on the CUMULANTS analysis that converts the intensity autocorrelation functions to intensity weighted particle mean Brownian diffusion motion (and polydispersity index). The hydrodynamic diameter is determined with Stokes-Einstein equation by assuming that the particles are spherical. Three measurements of each sample were run and all the experiments were done in duplicates.

2.3.3. Spectroscopy. A UV-Vis spectroscopy (Shimadzu UV-1601 PC, Shimadzu Corporation, Japan) was applied to monitor the absorbance of TiO₂-P25 particles. At the studied concentrations, the relative absorbance is highly consistent with the relative particle concentration. The test samples were
prepared in 20 mm quartz cuvettes. Absorbance of dispersed TiO$_2$ nanoparticles were measured at a wavelength of 378 nm every 5 min over the 300-min period. The detection limit of the method was about 1 mg/l. All the experiments were done as duplicates.

2.3.4. Electron microscopy. The TiO$_2$-P25 powder was imaged with a Field emission scanning electron microscopy (FESEM; JEOL JSM-6335F) operated at secondary mode. The optimal resolution of FESEM is 1.5 nm and its measurement uncertainty is approximately 1%. The elemental composition of the investigated powder was confirmed with an Energy-dispersive X-ray analysis (EDS). The detection limit of the EDS varied in the range of 0.1-0.5 % according to an analyte.

![FESEM image of titanium dioxide (P25-TiO$_2$) powder.](image)

Figure 1. FESEM image of titanium dioxide (P25-TiO$_2$) powder.

3. Results and discussion

3.1. Water quality parameters of natural water samples

The selected physicochemical water quality parameters are presented for two brackish water and two fresh water samples in Table 1. The brackish water samples was basic (pH ~ 8), whereas Iso Lehmälampi water sample was more acidic (pH ~ 5.0) than Simijärvi water sample (pH 6.1). The conductivity describing the ion strength was predictably much higher in brackish waters than in fresh waters. The concentration of total organic carbon (TOC) varied in a relatively narrow range. The highest TOC concentration was measured in Iso Lehmälampi sample (6.1 mg/l) and the lowest in Simijärvi sample (4.1 mg/l). The water colour of the analysed water samples was consistent with the TOC concentration which reflects the content of natural organic matter. In addition, the fresh waters were analysed for several elements and common nutrients. The concentrations of most abundant divalent ions were above 2-fold higher in Simijärvi than in Iso Lehmälampi.

3.2. Aggregation of TiO$_2$ nanoparticles

The stability of TiO$_2$-P25 particles were tested at two initial concentrations of 100 mg/l and 1 mg/l (Figure 2). As expected, the agglomeration rate was very high in high ion strength conditions, i.e. brackish water samples. In three minutes, that is the time between the spiking and the first measurement, the intensity weighted mean hydrodynamic diameter had already increased from 200 nm to 1500 nm at the initial concentration of 100 mg/l. During the 60-min experiment, the mean hydrodynamic diameter increased close to 3000 nm in brackish waters. Contrary to brackish waters, there was difference in the agglomeration rates between the two fresh water samples. After the immediate increase of particle size (from 200 nm to 500 nm), the intensity weighted mean
hydrodynamic diameter grew only slightly in Iso Lehmälampi water, whereas the mean particle size in Simijärvi sample was approximately 1600 nm at the end of 60-min experiment. The higher conductivity and concentration of divalent ions as well as lower TOC in Simijärvi sample may result in the faster agglomeration than in Iso Lehmälampi. In addition, the pH value of Simijärvi sample may be close to the isoelectric point of TiO$_2$-P25 particle dispersion, which would also favour the agglomeration.

Table 1. Physicochemical water quality characteristics of the tested natural waters.

|                      | Långskär | Tvärminne | Simijärvi | Iso Lehmälampi |
|----------------------|----------|-----------|-----------|----------------|
| Al (µg/l)            | –        | –         | 73        | 160            |
| Alcalinity (mmol/l)  | –        | –         | 0.011     | 0.012          |
| Ba (µg/l)            | –        | –         | 6.3       | 4.7            |
| Ca (mg/l)            | –        | –         | 1.7       | 0.7            |
| Cl (mg/l)            | –        | –         | 1.8       | 1.5            |
| Water colour (mg Pt/l)| 15       | –         | 15        | 50             |
| COD$_{Mn}$ (mg/l)    | –        | –         | 2.7       | 5.1            |
| Conductivity (mS/m)  | 978      | 704       | 2.7       | 1.9            |
| F (µg/l)             | –        | –         | 41        | 47             |
| Fe (µg/l)            | –        | –         | 24        | 400            |
| K (mg/l)             | –        | –         | 0.3       | 0.4            |
| Mg (mg/l)            | –        | –         | 0.7       | 0.3            |
| Mn (µg/l)            | –        | –         | 7.5       | 15             |
| Na (mg/l)            | –        | –         | 1.5       | 1.1            |
| N-NH$_4$ (µg/l)      | <2       | –         | <2        | 48             |
| N-NO$_2$+NO$_3$ (µg/l)| <2       | –         | 154       | 41             |
| N-total (µg/l)       | 350      | –         | 300       | 310            |
| Dissolved O2 (µg/l)  | 13.4     | –         | 11.7      | 4.9            |
| pH                   | 8.1      | 8.0       | 6.1       | 5.0            |
| P-PO$_4$ (µg/l)      | 3        | –         | <2        | <2             |
| P-total (µg/l)       | 25       | –         | 3         | 8              |
| Salinity (%)         | 5.55     | 3.89      | –         | –              |
| SiO$_2$ (mg/l)       | 0.49     | 0.52      | 2.5       | 1.6            |
| SO$_4$ (mg/l)        | –        | –         | 5.4       | 2.7            |
| Sr (µg/l)            | –        | –         | 15        | 5.3            |
| TIC (mg/l)           | –        | –         | <0.5      | 3.0            |
| TOC (mg/l)           | 4.2      | 5.6       | 4.1       | 6.1            |
| Turbidity (FNU)      | 1.9      | 4.7       | 0.40      | 1.1            |

At concentration of 1 mg/l, the initial particle size was close to that of stock dispersion and it remained stable over 60-min period in fresh water samples. The aggregates formed in brackish waters but the intensity weighted mean particle size was only about 400 nm at the end of 60-min experiment. A comparison between the agglomerate size in the two concentrations shows that the concentration plays an important role in the particle aggregation. This is due to the decreasing distance between the suspended particles at the increasing concentrations, which results in the increased probability of collisions between particles. Therefore, to get more realistic understanding on the environmental fate of engineered nanoparticles in different environmental samples, some of the experiments should be conducted close to the predicted environmental levels in the future studies. However, this requires the development of more sensitive analytical methods.
3.3. Deposition of TiO$_2$ nanoparticles

The TiO$_2$ concentration was monitored over a 5-h period by using the UV-Vis spectrophotometer. As the formation of aggregates indicated, the dispersed particle concentration decreased strongly in brackish waters. At the concentration of 100 mg/l in brackish waters, the relative absorbance dropped down to 20% of initial absorbance in 5 hours. The relative absorbance showed a similar trend in both brackish waters: first it decreased slowly, followed by a steep drop of absorbance between 80 and 100 min and then the decrease slowed down. The similar deposition pattern was shown earlier for reactive nanosized iron particles [12]. The steep drop in the relative absorbance is likely due to the gravitational settling of large aggregates. The sedimentation lowers the concentration of dispersed particles and thus the settling slows down. At the higher concentration, the relative absorbance decreased in Simijärvi water, but it remained stable in Iso Lehmälampi water over the whole 5-hour experiment. The stable particle size and absorbance in Iso Lehmälampi water indicate that the deposition observed in other water samples was due to gravitational settling and the deposition on the walls due to the particle diffusion was minor. The aggregation and deposition observations support strongly each other.
The deposition was strongly dependent on the particle concentration. Since the detection limit of UV-Vis spectroscopy for the TiO$_2$ particles was 1 mg/l, the lower concentration for deposition experiments had to be chosen as 10 mg/l. At the lower concentration, the deposition rate was clearly lower in brackish waters. During the 5-hour experiments, the relative absorbance decreased about 20% in the brackish waters and about 5% in Simijärvi water, whereas the relative absorbance remained stable in Iso Lehmalampi water.

4. Summary and conclusions
Nanoparticle transport, persistence and bioavailability in the environment are essential aspects to consider in risk assessment and management. The stabilization of nanoparticles in aquatic environment is the sum of the intrinsic properties of material itself (e.g. size, surface chemistry and charge and hydrophilicity) and the physicochemical characteristics of receiving environment (e.g. pH, ionic strength, ratio of divalent to monovalent ions and organic matter). As shown in this study, the particle concentration also plays an important role. Nanoparticles that undergo aggregation will sediment and thus become less mobile. Consequently, the released engineered nanoparticles occur close to their sources and benthic organisms have higher potential to expose these aggregated nanoparticles. On the other hand, the stabilized nanoparticles are dispersed over larger area and may have impact on aquatic organisms. The brackish water samples tested in this study destabilized the TiO$_2$ particle dispersion which resulted in the remarkable sedimentation within a few hours. The fresh water led either the destabilisation or stabilisation of TiO$_2$ particles depending on the water quality variables. While the environmental concentrations of TiO$_2$ nanoparticles will probably be lower than those tested in this study, the initial source may discharge at these levels. The further studies should focus on the nanoparticle concentrations close to the PEC-values, which challenges the current analytical techniques.

Acknowledgements
The authors wish to thank the Finnish Standards Association SFS and the association of Maa- ja Vesitekniikan Tuki ry for financial support. In addition, Ms. Heljä Haapala is acknowledged for her technical help during the experiments and the laboratory staff of SYKE Environment measurement and testing group for the analysis of water quality.

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