Behavior of TiO$_2$ Nanoparticles in Different Soil Suspensions

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**Key Words:** aggregate stability in soil solution, soil suspensions, TiO$_2$ nanoparticles

**Abstract**

The emergence of nanotechnology can cause an exponentially and uncontrollably emission in the environment (air, water and soil ecosystems) of the nanomaterials that are produced and used. The effects of these products on the environment and on human health are unknown, and precautionary measures are warranted until possible risks have been elucidated. In particular, fate and behavior of nanomaterials in soils and groundwater must be investigated. We studied the behavior of nanoparticles in suspensions of three different Italian soils. Aliquots of TiO$_2$-nanoparticle suspensions with and without soil were collected periodically after their preparation, and monitored for aggregate size distribution and Ti concentration. Experimental results suggest that the soil properties affect the behavior of TiO$_2$-NPs, as they are particularly influenced by the dissolved organic matter as well as the ionic strength.

**Introduction**

Engineered nanomaterials are materials designed at the nanometer level (molecular level). The significant differences in the properties of nano and bulk materials are due to the increased surface area and new quantum effects. The increase of applications of nanomaterials and consequent increased production are expected to cause exponentially and uncontrollably emissions in the environment (air, water and soil ecosystems). More and more, the study of the fate and impact in the environment is becoming important due to the gap of knowledge about transport in and between environmental compartments and chemical behavior in the environment, specially for soil ecosystem (Klain et al., 2008). TiO$_2$-nanoparticles (TiO$_2$-NPs) are a good example of a nanomaterial that has been accepted as having many properties useful for a wide range of applications, from ‘self-cleaning’ surfaces to cosmetics (Woodrow Wilson database). It is one of the nanomaterials of major industrial production thus the need of understanding its transport and diffusion in different soils. This study shows the preliminary results on the behavior of TiO$_2$-NPs in suspensions of three different Italian soils.

**Materials and Methods**

Three soils were collected to a depth of 20 cm, air dried and sieved to 2 mm. TiO$_2$-NPs were purchased from Sigma-Aldrich (USA) with an anatase phase purity of 99.7%, specific surface area 200-220 m$^2$/g and average particle size of 25 nm. TiO$_2$-NPs suspensions with and without soils were obtained by 24 h shaking of TiO$_2$-NPs, soil and milli-Q water in the ratio 1:25:500, respectively. Mixtures were transferred into columns (time 0) and allowed to settle undisturbed for nine days. Aliquots of suspensions were collected periodically at day 0, 3, 6 and 9, and analyzed for aggregate size distribution and Ti concentration. The aggregate size distributions were determined using a laser particle size analyzer (Mastersizer 2000, Malvern); the concentration of Ti was determined using an ICP-OES (Liberty Axial, Varian) after sample drying and digestion in H$_2$SO$_4$/NH$_4$SO$_4$ solution.

**Results and Discussion**

The soils differed significantly for particle size distribution and organic matter (OM) content (Table 1). As expected, the capacity of cationic exchange was significantly higher in the two soils richer in clay and in organic carbon. Moreover, values of electrical conductivity (EC) suggest that ionic strength is higher in sandy and lower in clayey soil.

<table>
<thead>
<tr>
<th>Soil</th>
<th>pH</th>
<th>CEC</th>
<th>Sand</th>
<th>SiO$_4$</th>
<th>Al$_2$O$_3$</th>
<th>TiO$_2$</th>
<th>OM</th>
<th>EC</th>
<th>mm/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>8.0</td>
<td>41.6</td>
<td>23.9</td>
<td>6.3</td>
<td>12.8</td>
<td>0.16</td>
<td>714</td>
<td>458</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>6.1</td>
<td>52.3</td>
<td>37.7</td>
<td>27.9</td>
<td>34.3</td>
<td>9.0</td>
<td>458</td>
<td>728</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>8.8</td>
<td>14.4</td>
<td>90.3</td>
<td>6.6</td>
<td>3.1</td>
<td>0.15</td>
<td>814</td>
<td>458</td>
<td></td>
</tr>
</tbody>
</table>

Ti concentration in the suspension without soil (Table 2) showed an abrupt decrease, and remained constant from day 3 to 9. Soil suspensions without TiO$_2$-NPs showed a similar trend, but a constant concentration was found after day 6. Soil I with TiO$_2$-NPs showed Ti concentrations similar to soil alone at days 3 to 9. In soil II with TiO$_2$-NPs Ti concentration was significantly higher than in soil alone at all sampling times. Soil III with TiO$_2$-NPs showed Ti concentration lower than soil alone since day 3. The relative higher OM content in soil II and probably higher dissolved organic matter could contribute to the stabilization of TiO$_2$-NPs in soil solution as it can acts as a kind of surfactant reducing the collision and agglomeration between particles, giving a sterically stabilized system. This finding is consistent with the mechanism of stabilization of colloidal particles by steric interaction that was showed to be valid in case of natural organic matter (Tandros, 2007, Hyung et al., 2007, Gisalusdini et al., 2007). In Soil III the higher settling of TiO$_2$-NPs could be attributed to higher ionic strength and pH. Several
authors (Tandros, 2007; Kleine et al., 2008) reported that NPs quickly aggregated with high ionic strength that compressed the diffuse double layer, causing the fast settling of NPs.

Table 2 Concentration of Ti (mg/l) in the different soil suspensions at each sampling time. Ti concentration was measured using ICP-AES.

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>0</th>
<th>3</th>
<th>6</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil I</td>
<td>1072</td>
<td>1059</td>
<td>1054</td>
<td>1045</td>
</tr>
<tr>
<td>Soil II</td>
<td>1347</td>
<td>1344</td>
<td>1339</td>
<td>1334</td>
</tr>
<tr>
<td>Soil III</td>
<td>1567</td>
<td>1564</td>
<td>1559</td>
<td>1554</td>
</tr>
</tbody>
</table>

At time 0, the aggregate size distribution of TiO$_2$-NPs suspensions was between 0.15 and 10 μm with a peak at 2.7 μm, while the three soils gave distributions consistent with their textural classification. Suspensions with TiO$_2$-NPs and soils gave distributions where the contribution of the two components were clearly recognizable, particularly in the case of sandy soil (Figure 1). These data suggest a low interaction between TiO$_2$-NPs and soil particles, at least in terms of aggregation or physical rearrangement. After day 3 all the suspensions showed a similar pattern, with a peak around 0.7 μm, suggesting that TiO$_2$-NPs were still present as aggregates.

Conclusion
The present study provides evidence that the soil properties affect the behavior of TiO$_2$-NPs, specially influenced by the OM content and ionic strength.

References


Figure 1. Size distribution of suspended particles at time 0.

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