Potential transformation processes of quantum dots and their colloidal stability in complex aqueous matrices

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Engineered nanomaterials (ENMs) vs. their bulk counterparts

Fig. Nano-SiO$_2$ dispersed in leachates (right) and in MeOH (below), © DNB-T-BOKU

ENMs interact with naturally-occurring substances leading to transformations

Gravity

Brownian motion

Forces
Motivation of this study

• QDs are already available in **display technologies (QLEDs)** and other electronics due to their outstanding optical properties

• **Little information** at the point-of-manufacturing and, in particular, at the end of their useful life

• Many material flow models indicate that ENMs accumulate in waste streams and landfills

• Very little is known about **ENM transport and fate during landfilling**
Are landfills environmental sinks?

Which landfill parameters (e.g. DOC, pH, I etc.) have an influence on ENM mobility?

How can we differentiate ENMs from naturally-occurring nanomaterials?
Are quantum dots (QDs) applicable nanoscale tracer materials?

- **Hypothesis**: Nanotracers, where size, shape, and surface properties can be controlled. QDs are applicable model nanoparticles to distinctively trace their transport and fate in complex waste matrices.

- **Worst case assumptions**:
  - Persistent ENMs and high mobility
  - No natural counterparts
  - Already present/dispersed in five different landfill leachates that vary in DOC-content, pH, ionic strengths etc.
• Two different types of QDs:
  – N-Acetyl-L-cysteine (NAC) capped CdTe/CdS are hydrophilic (“NAC-QDs”)
  – Triocylphosphine/Triocylphosphine oxide (TOP/TOPO) capped CdSe/ZnS are hydrophobic → steric stabilization via amphiphilic non-ionic surfactant (“Brij®58-QDs”)

Fig.: Size-dependent colour of QDs and their emission spectra in Zrazhevskiy P., 2009: DOI: 10.1039/b915139g
Materials and methods: characterization and QD-spiking

• Characterization methods:
  – TEM → geometric diameter
  – DLS → hydrodynamic diameter
  – UV/VIS & fluorescence spectroscopy → spectroscopic fingerprints (first excitonic and emission peak)
  – HR-ICP-MS for trace metal concentration in leachates

• Spiking method:
  – QDs in powder form → preparation of stock solution (1 mg/mL) → dispersion of aliquots in 5 x 3 leachate samples with fixed concentrations
Potential transformation processes are directly related to QD‘s optical properties

Fig.: Part et al. XXXX, The long-term fate of two differently, sterically stabilized quantum dots in landfill leachates and their potential transformation processes, submitted and currently under review
Results: background characterization

- Emission-excitation-matrix spectroscopy measurements showed that all leachates predominantly contained **fulvic** and **humic acids**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Leachate 1</th>
<th>Leachate 2</th>
<th>Leachate 3</th>
<th>Leachate 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH (initial)</td>
<td>8.3</td>
<td>8.0</td>
<td>7.8</td>
<td>8.3</td>
</tr>
<tr>
<td>pH after dilution (a)</td>
<td>8.6</td>
<td>8.5</td>
<td>8.7</td>
<td>8.6</td>
</tr>
<tr>
<td>pH after dilution &amp; QD-spiking</td>
<td>8.6</td>
<td>8.5</td>
<td>8.7</td>
<td>8.6</td>
</tr>
<tr>
<td>electrical conductivity (20°C) [mS cm⁻¹]</td>
<td>14.9</td>
<td>20.3</td>
<td>2.1</td>
<td>14.8</td>
</tr>
<tr>
<td>DOC (initial) [mg L⁻¹]</td>
<td>620 ± 0.8%</td>
<td>1085 ± 0.5%</td>
<td>66 ± 5.0%</td>
<td>913 ± 4.4%</td>
</tr>
<tr>
<td>DOC after dilution (a) [mg L⁻¹]</td>
<td>62 ± 0.8%</td>
<td>109 ± 0.5%</td>
<td>7 ± 5.0%</td>
<td>91 ± 4.4%</td>
</tr>
<tr>
<td>NH₄⁺ [mg L⁻¹]</td>
<td>454</td>
<td>1180</td>
<td>82</td>
<td>827</td>
</tr>
<tr>
<td>NO₃⁻ [mg L⁻¹]</td>
<td>75</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td>20</td>
</tr>
<tr>
<td>SO₄²⁻ [mg L⁻¹]</td>
<td>74</td>
<td>24</td>
<td>13</td>
<td>56</td>
</tr>
<tr>
<td>Fe⁵⁶ [μg L⁻¹]</td>
<td>970 ± 5%</td>
<td>4000 ± 5%</td>
<td>&lt; LOD</td>
<td>not measured</td>
</tr>
<tr>
<td>Cu⁶⁵ [μg L⁻¹]</td>
<td>42 ± 5%</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td>not measured</td>
</tr>
<tr>
<td>Zn⁶⁶ [μg L⁻¹]</td>
<td>72 ± 5%</td>
<td>&lt; LOD</td>
<td>41 ± 5%</td>
<td>not measured</td>
</tr>
<tr>
<td>Se⁸² [μg L⁻¹]</td>
<td>87 ± 5%</td>
<td>74 ± 5%</td>
<td>21 ± 5%</td>
<td>not measured</td>
</tr>
<tr>
<td>Cd¹¹¹ [μg L⁻¹]</td>
<td>4.0 ± 5%</td>
<td>3.0 ± 5%</td>
<td>3.0 ± 5%</td>
<td>not measured</td>
</tr>
<tr>
<td>Tc¹²⁵ [μg L⁻¹]</td>
<td>&lt; LOD</td>
<td>5.0 ± 5%</td>
<td>&lt; LOD</td>
<td>not measured</td>
</tr>
</tbody>
</table>

Table: Part et al. XXXX, The long-term fate of two differently, sterically stabilized quantum dots in landfill leachates and their potential transformation processes, submitted and currently under review
Results: assessment of long-term stability and behavior of “Brij®58-QDs”

- Spectroscopic fingerprints were detectable for at least 180 days → indicate high colloidal stability and mobility
- PEG coating prevent physisorption of DOC for 56 days → partial sedimentation

Fig: Part et al. XXXX, The long-term fate..., submitted and currently under review
Results: assessment of long-term stability and behavior of “NAC-QDs”

- At low DOC: fingerprints were traceable for 6 months → high colloidal stability
- Adsorption of dissolved metal ions (i.e. Cd$^{2+}$, Zn$^{2+}$) → further surface passivation (kinetics mainly depend on temperature)

Fig: Part et al. XXXX, The long-term fate…, submitted and currently under review
Results: assessment of long-term stability and behavior of “NAC-QDs”

- At high DOC: fluorescence peak disappeared after 14 days, but first excitonic peak not
- chemisorption and ligand exchange of NAC for fulvic/humic acids → further steric stabilization
Conclusions and recommendations

• Sterically stabilized ENMs can be colloidally stable and very mobile under prevailing environmental conditions depending on their surface properties/densities, temperature, residence time, DOC- and dissolved metal content (pH in leachates retained constant → no significant influence)

• QDs with low Mw capping agents (e.g. NAC) mainly underwent chemical transformation

• QDs with high Mw capping agents (e.g. Brij®58) mainly underwent physisorption processes

• Waste incineration is highly recommended to decrease their colloidal stability in liquid wastes
Conclusions and outlook

• **Fluorescent ENMs** or **QDs** are **applicable nanotracers** and are going to be used for further transport and toxicity studies

• **Spectroscopic fingerprints** allow distinctive tracing and differentiation from naturally-occurring nanoscale substances

• QDs can be differently **surface modified** (e.g. using ZnO, SiO$_2$ or TiO$_2$)

• QDs **can mimic other nanoparticles** to a certain extent regarding size, density, shape and surface properties
Thank you for your attention!

For further questions, you can also send me an email:

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Figures: further fate and toxicity studies on, for example, magnetic and ZnO-coated QDs are currently conducted at the BOKU; left: CLSM image of PEGylated QDs dispersed in cell line A549; middle left: Fe doped QDs; middle right: ZnO coated, Cd-free QDs; right: synthesis of organo-soluble QDs used as photostable, inorganic dye.
Thanks to all co-authors!

Preparation of water-soluble, PEGylated, mixed-dispersant quantum dots, with a preserved photoluminescence quantum yield†
C. Zaba,‡a O. Bixner,‡ap F. Part,‡a C. Zafiu,‡c C.-W. Tan‡a and E.-K. Sinner*‡a

Current limitations and challenges in nanowaste detection, characterisation and monitoring
Florian Part ‡a, Gudrun Zecha ‡a, Tim Causon ‡b, Eva-Kathrin Sinner ‡c, Marion Huber-Humer ‡a,*

Editorial
Engineered nanomaterials in waste streams
Traceability of fluorescent engineered nanomaterials and their fate in complex liquid waste matrices*
## Additional information: QD-sizes

<table>
<thead>
<tr>
<th>QD-species</th>
<th>NAC-QDs in water</th>
<th>TOP/TOPO-QDs in chloroform</th>
<th>Brij®58-QDs in water</th>
</tr>
</thead>
<tbody>
<tr>
<td>R&lt;sub&gt;Core&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt;</td>
<td>~ 1.2</td>
<td>~ 2.0</td>
<td>~ 2.0</td>
</tr>
<tr>
<td>R&lt;sub&gt;Shell&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</td>
<td>~ 0.6</td>
<td>~ 0.6</td>
<td>~ 0.6</td>
</tr>
<tr>
<td>R&lt;sub&gt;Ligand&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt;</td>
<td>~ 0.9</td>
<td>~ 1.0</td>
<td>~ 1.0</td>
</tr>
<tr>
<td>R&lt;sub&gt;Surfactant&lt;/sub&gt;</td>
<td>-</td>
<td>-</td>
<td>~ 7.0</td>
</tr>
<tr>
<td>R&lt;sub&gt;Total&lt;/sub&gt;</td>
<td>~ 2.7</td>
<td>~ 3.6</td>
<td>~ 10.6</td>
</tr>
</tbody>
</table>

**Geometric radii [nm]**

### Hydrodynamic diameters [nm]<sup>d</sup>

<table>
<thead>
<tr>
<th>Peak 1</th>
<th>15.7 ± 4.0</th>
<th>8.7 ± 1.3</th>
<th>141.8 ± 85.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intensity [%]</td>
<td>0.7</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Mass [%]</td>
<td>24.8</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Peak 2</td>
<td>91.3 ± 53.7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Intensity [%]</td>
<td>99.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mass [%]</td>
<td>75.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P&lt;sub&gt;d&lt;/sub&gt;I&lt;sup&gt;e&lt;/sup&gt;</td>
<td>0.31</td>
<td>0.20</td>
<td>0.18</td>
</tr>
</tbody>
</table>


<sup>a</sup> core radii of CdTe and CdSe QDs calculated according to Rogach et al. (2007) and Yu et al. (2003), respectively

<sup>b</sup> shell thickness based on Pons et al. (2006)

<sup>c</sup> based on estimations from the molar volume

<sup>d</sup> HDD measured using DLS at 21°C

<sup>e</sup> nanoparticles are monodisperse when polydispersity index (P<sub>d</sub>I) ≤ 0.2
Additional information: Summary of hypotheses and assumption

• QD-behaviour and **aggregation kinetics** in environmental samples predominantly depending on dissolved organic content (DOC)

• Nano-specific fluorescence properties change:
  – when **DOC interact with QDs** → sorption, particle aggregation or complexation lead to decrease in fluorescence intensity
  – when **QDs decompose** → leaching of heavy metal ions (dissolution of particle core) or oxidation lead to decrease in fluorescence intensity and absorbance
  – **No change** in fluorescence indicate colloidal stability