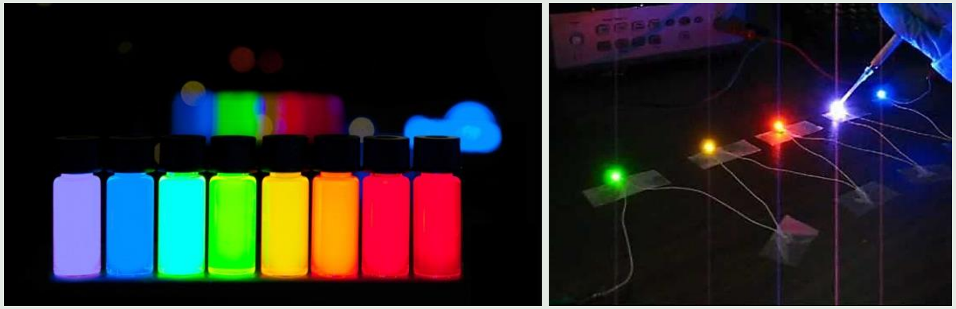
International Conference on Health & Safety issues related to Nanomaterials, Nanosafe 2016
November 7-10, 2016 – Grenoble, France

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



QDs in LEDs, © Plasma Chem GmbH

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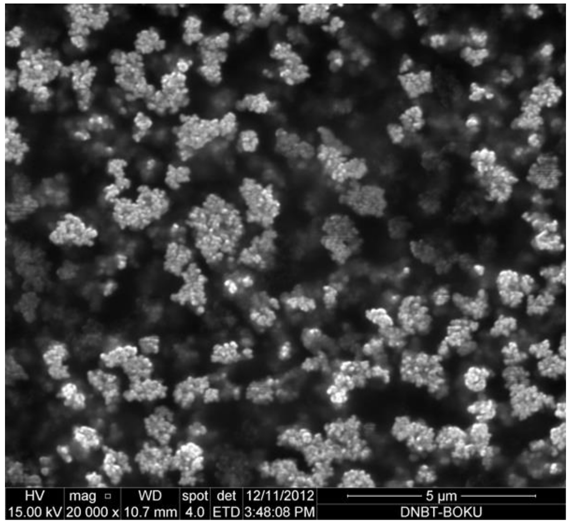
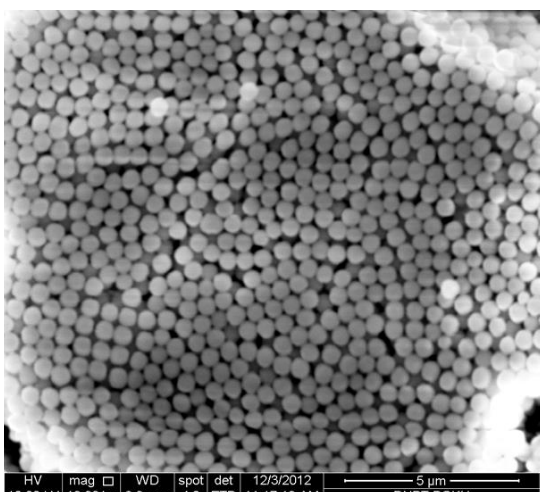
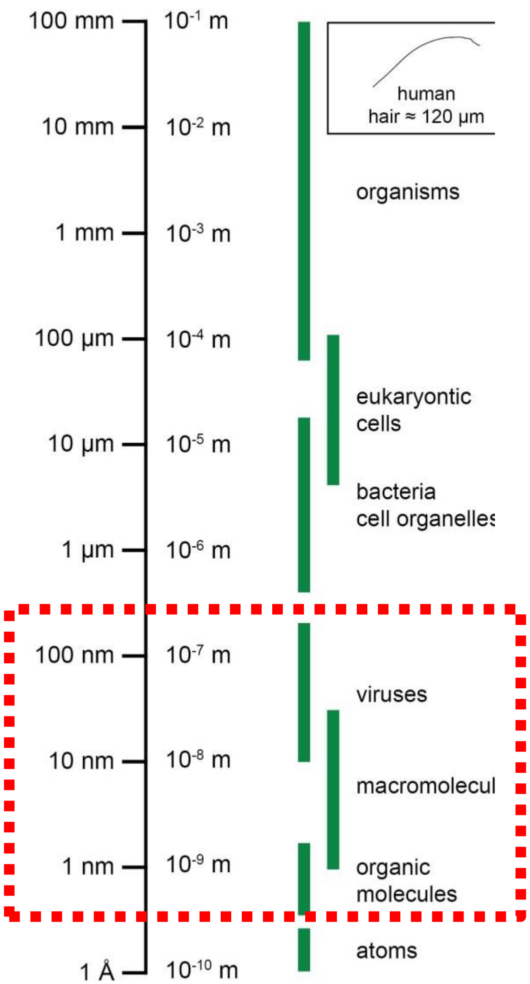
Engineered nanomaterials (ENMs) vs. their bulk counterparts

Fig. **Nano-SiO_2** dipsersed in leachates (right) and in MeOH (below), © DNBT-BOKU

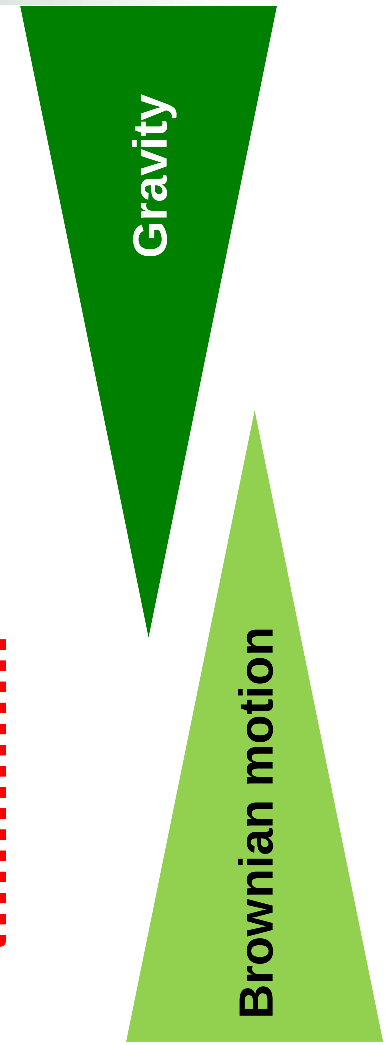




ENMs interact with naturally-occurring substances leading to transformations

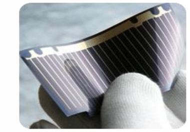


Forces



Motivation of this study

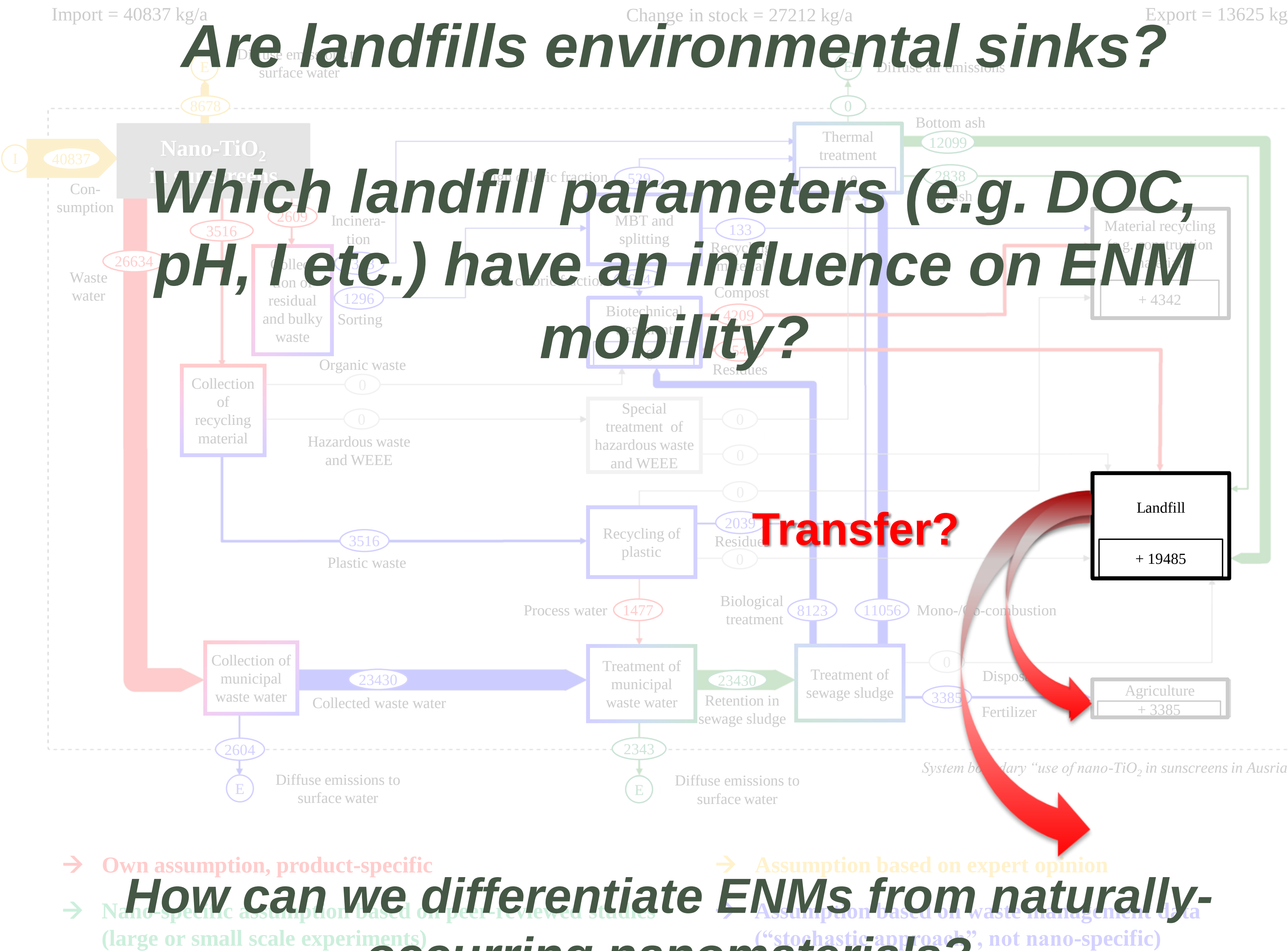

Sony Bravia^{TM} XBR 4K TV


Thin Film Solar Cell, © SONO TEK

- 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?

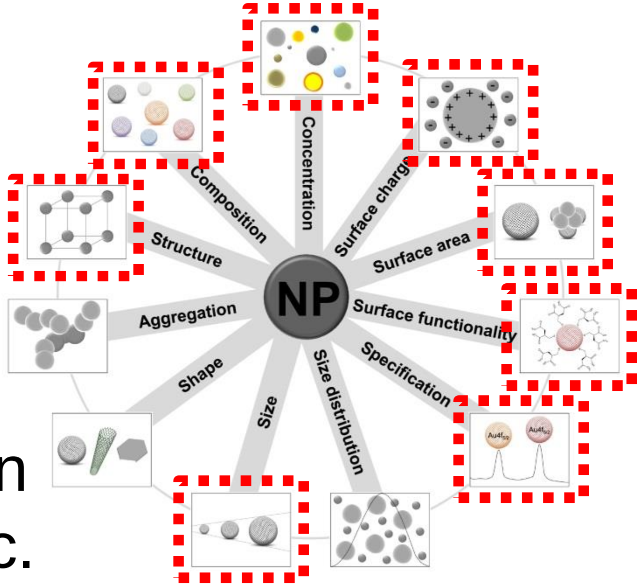
Which landfill parameters (e.g. DOC, pH, I etc.) have an influence on ENM mobility?



How can we differentiate ENMs from naturally-occurring nanomaterials?

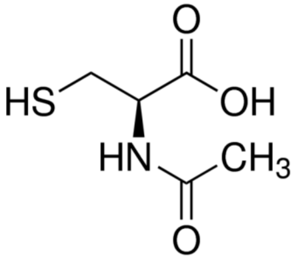
Are quantum dots (QDs) applicable nanoscale tracer materials?

- **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.

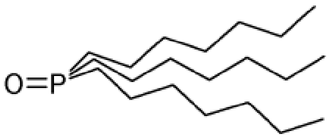


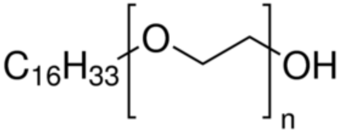
Materials and methods: synthesis and surface modification

- Two different types of QDs:
  - *N*-Acetyl-*L*-cysteine (NAC) capped CdTe/CdS are **hydrophilic** (“***NAC-QDs***”)



  - Trioctylphosphine/Trioctyl-phosphine oxide (TOP/TOPO) capped CdSe/ZnS are hydrophobic → steric stabilization via amphiphilic **non-ionic surfactant** (“***Brij®58-QDs***”)





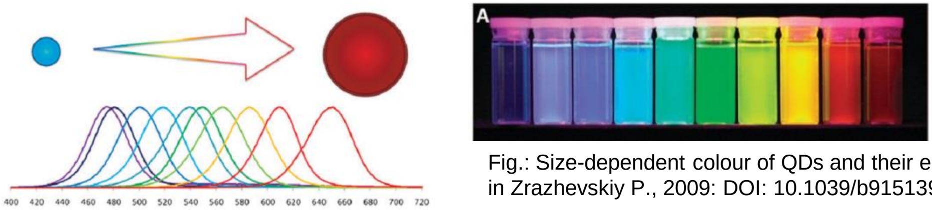


Fig.: Size-dependent colour of QDs and their eimission spectra in Zrazhevskiy P., 2009: DOI: 10.1039/b915139g

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

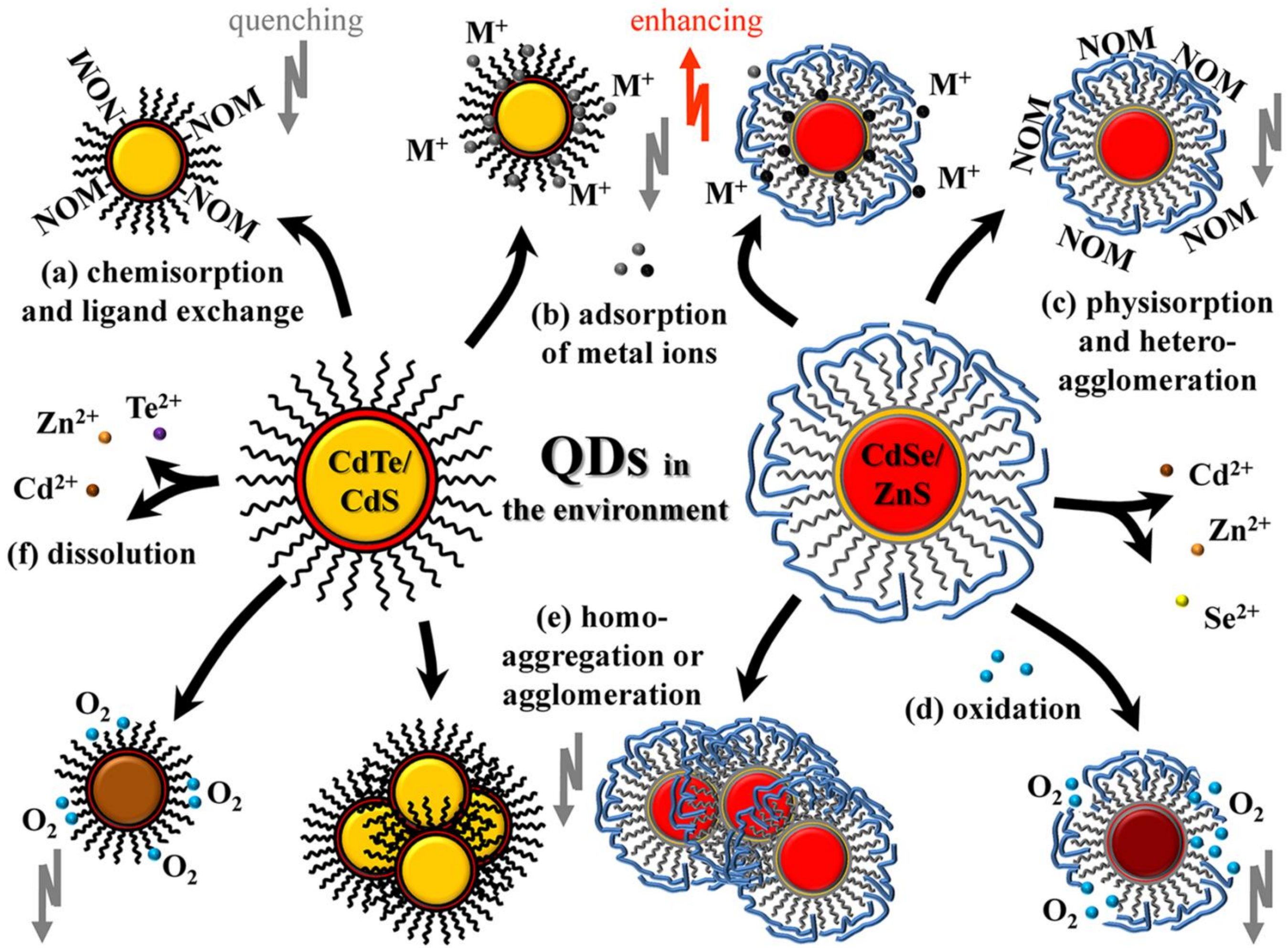


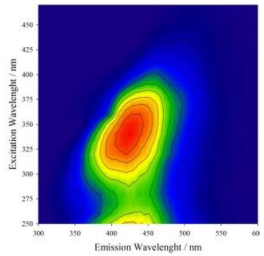
Fig.: Part et al. XXXX, The long-term fate of two differently, sterically stabilized quantum dots in landfill leachates and their potential transformation processes, *submitted and currently under review*

Results: background characterization

Sample		Leachate 1	Leachate 2	Leachate 3	Leachate 4
pH (initial)		8.3	8.0	7.8	8.3
pH after dilution[(a)]		8.6	8.5	8.7	8.6
pH after dilution & QD-spiking		8.6	8.5	8.7	8.6
electrical conductivity (20°C)	[mS cm^{-1}]	14.9	20.3	2.1	14.8
DOC (initial)	[mg L^{-1}]	620 ± 0.8%	1085 ± 0.5%	66 ± 5.0%	913 ± 4.4%
DOC after dilution[(a)]	[mg L^{-1}]	62 ± 0.8%	109 ± 0.5%	7 ± 5.0%	91 ± 4.4%
NH_4^+	[mg L^{-1}]	454	1180	82	827
NO_3^-	[mg L^{-1}]	75	< LOD	< LOD	20
SO_4^{2-}	[mg L^{-1}]	74	24	13	56
Fe^{56}	[µg L^{-1}]	970 ± 5%	4000 ± 5%	< LOD	not measured
Cu^{65} inital	[µg L^{-1}]	42 ± 5%	< LOD	< LOD	not measured
Zn^{66}	[µg L^{-1}]	72 ± 5%	< LOD	41 ± 5%	not measured
Se^{82}	[µg L^{-1}]	87 ± 5%	74 ± 5%	21 ± 5%	not measured
Cd^{111}	[µg L^{-1}]	4.0 ± 5%	3.0 ± 5%	3.0 ± 5%	not measured
Te^{125}	[µg L^{-1}]	< LOD	5.0 ± 5%	< LOD	not measured

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*

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



Results: assessment of long-term stability and behavior of *"Brij®58-QDs"*

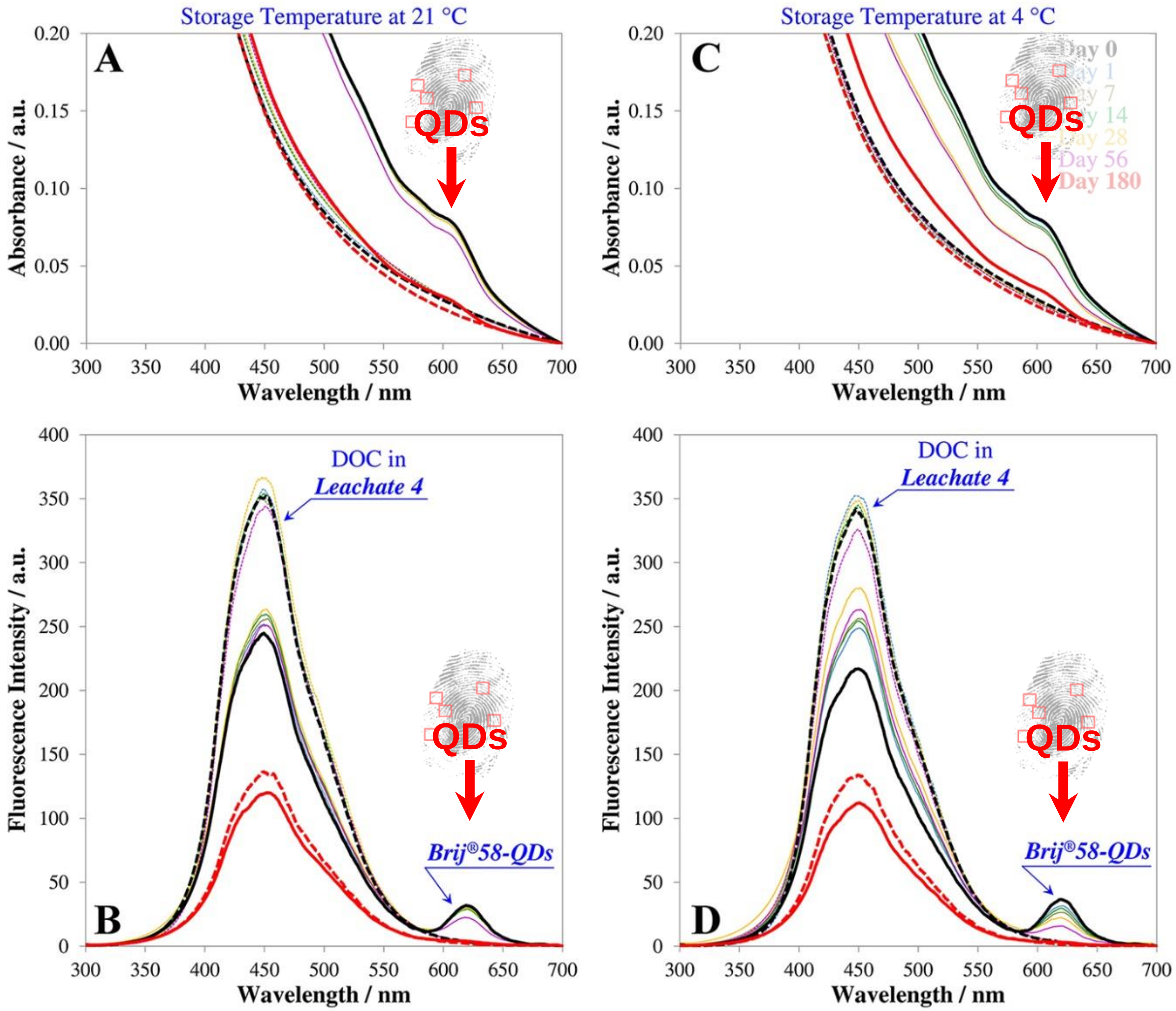


Fig: Part et al. XXXX, The long-term fate…, *submitted and currently under review*

- 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 sedi-mentation**

Results: assessment of long-term stability and behavior of "*NAC-QDs*"

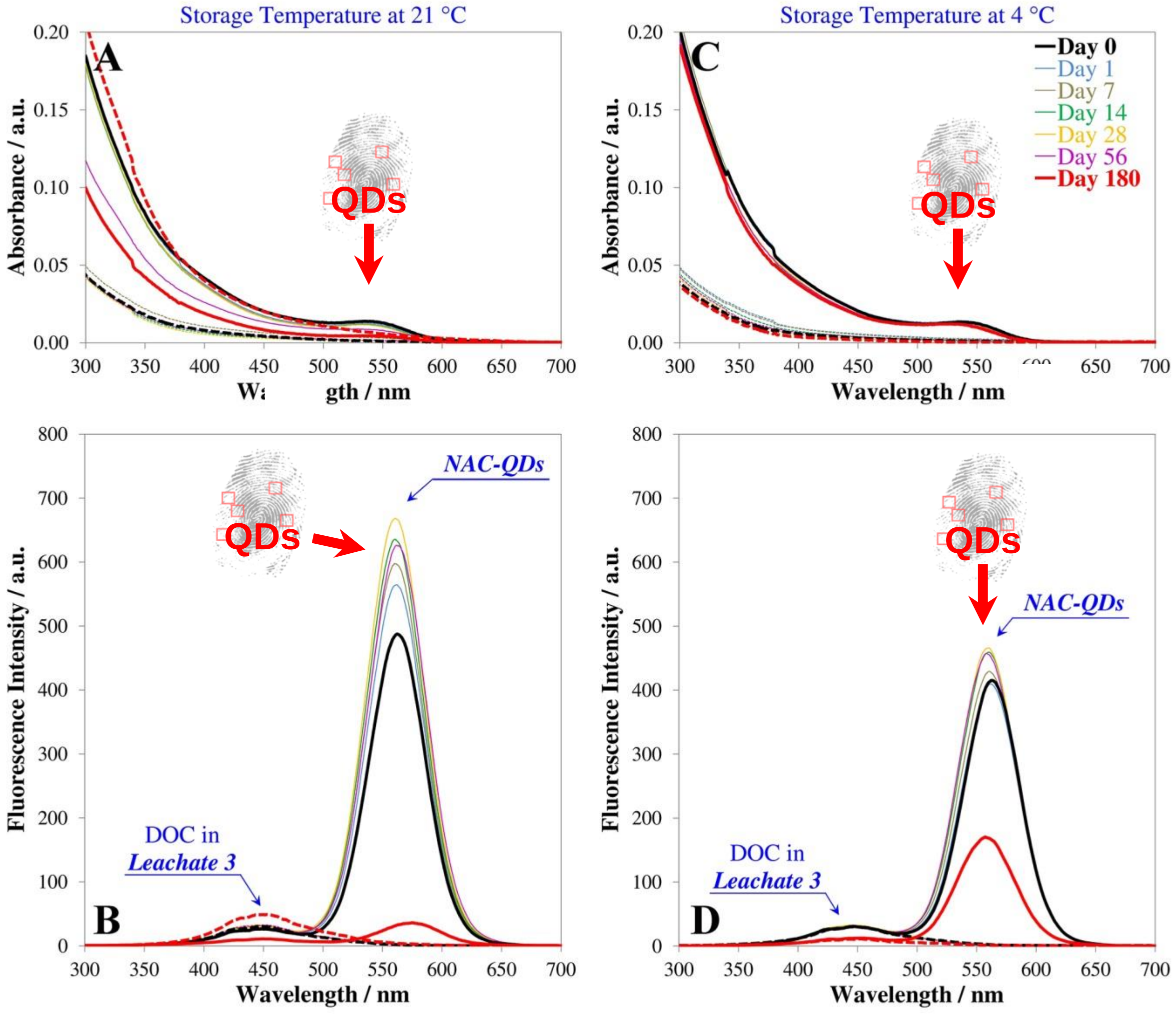


Fig: Part et al. XXXX, The long-term fate…, *submitted and currently under review*

- At **low DOC**: fingerprints were **traceable for 6 months** → high colloidal stability
- **adsorption** of dis-solved metal ions (i.e. Cd^{2+}, Zn^{2+}) → further **surface passivation** (kinetics mainly de-pend on temperature)

Results: assessment of long-term stability and behavior of “*NAC-QDs*”

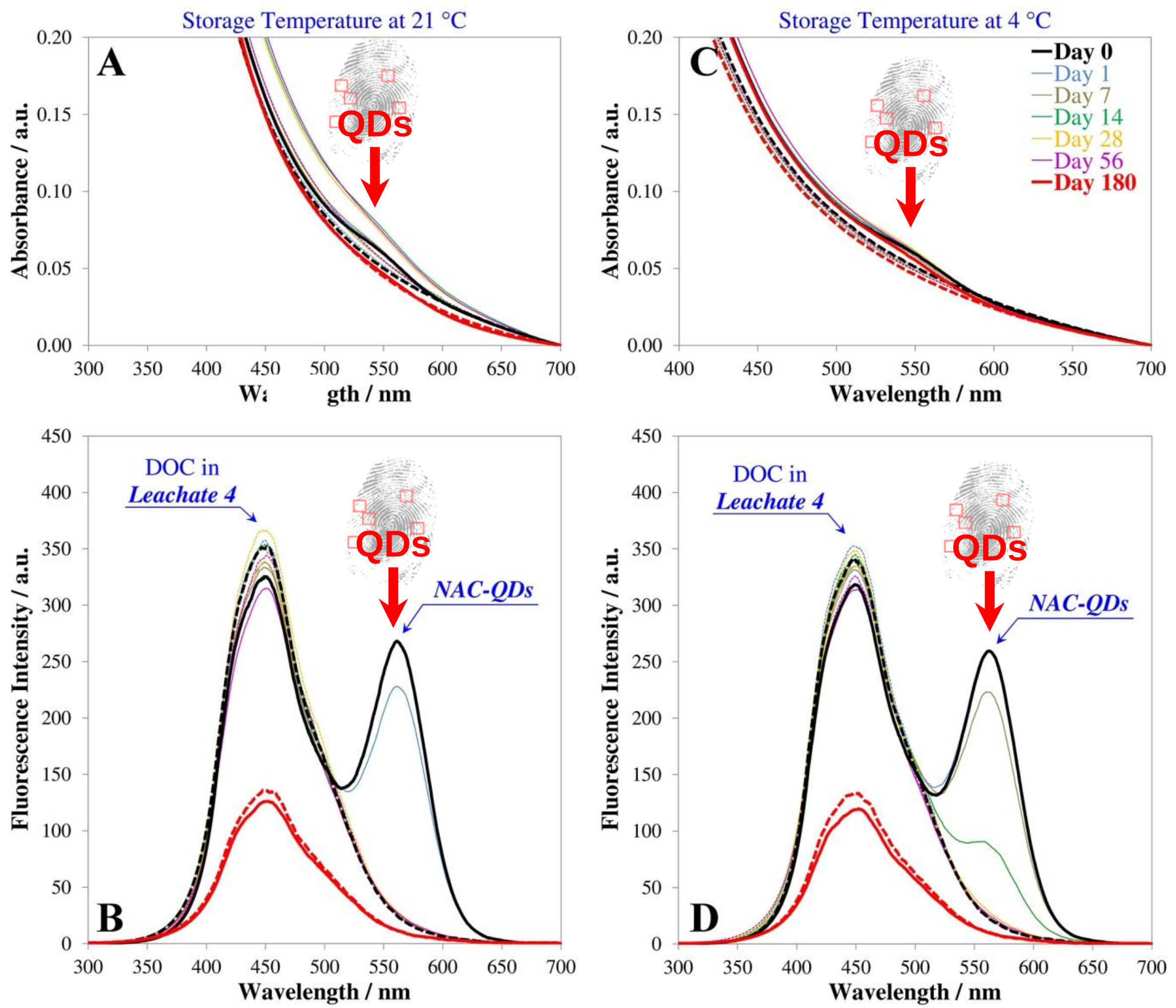


Fig: Part et al. XXXX, The long-term fate…, *submitted and currently under review*

- 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 stabi-lization**

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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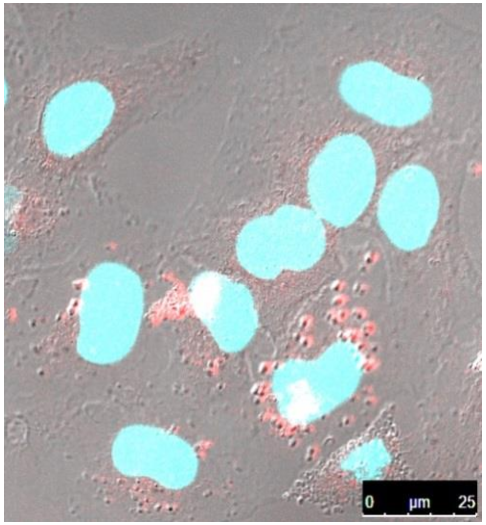

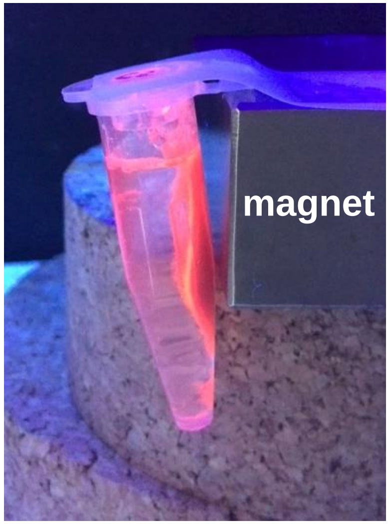

Figures: further fate and toxicity studies on, for example, magnetic and ZnO-coated QDs are currently conducted at the BOKU; left: CLSM image of PEGylated QDs dispersed in cell line A549; middle left: Fe doped QDs; middle right: ZnO coated, Cd-free QDs; right: synthesis of organo-soluble QDs used as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

Thanks to all co-authors!

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Cite this: *RSC Adv.*, 2016, **6**, 27068

Preparation of water-soluble, PEGylated, mixed-dispersant quantum dots, with a preserved photoluminescence quantum yield†

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Waste Management 43 (2015) 407–420

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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,*]

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Engineered nanomaterials in waste streams

Environmental Pollution 214 (2016) 795–805

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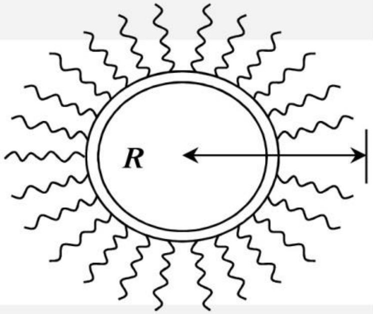
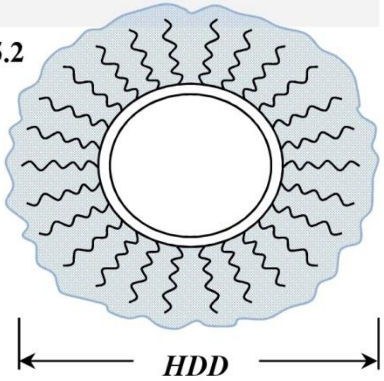
Traceability of fluorescent engineered nanomaterials and their fate in complex liquid waste matrices☆

Additional information: QD-sizes

QD-species	NAC-QDs in water	TOP/TOPO-QDs in chloroform	Brij®58-QDs in water
		Geometric radii [nm]	
R_{Core} [a]	~ 1.2	~ 2.0	~ 2.0
R_{Shell} [b]	~ 0.6	~ 0.6	~ 0.6
R_{Ligand} [c]	~ 0.9	~ 1.0	~ 1.0
$R_{Surfactant}$	-	-	~ 7.0
R_{Total}	**~ 2.7**	**~ 3.6**	**~ 10.6**
		Hydrodynamic diameters [nm] [d]	
Peak 1	**15.7 ± 4.0**	**8.7 ± 1.3**	**141.8 ± 85.2**
Intensity [%]	0.7	100	100
Mass [%]	24.8	100	100
Peak 2	**91.3 ± 53.7**	-	-
Intensity [%]	99.3	-	-
Mass [%]	75.2	-	-
PdI [e]	*0.31*	*0.20*	*0.18*





[a] core radii of CdTe and CdSe QDs calculated according to Rogach et al. (2007) and Yu et al. (2003), respectively

[b] shell thickness based on Pons et al. (2006)

[c] based on estimations from the molar volume

[d] HDD measured using DLS at 21°C

[e] nanoparticles are monodisperse when polydispersity index (*PdI*) ≤ 0.2

Table: Part, F., Zaba, C., Bixner, O., Zafiu, C., Hann, S., Sinner, E.K., Huber-Humer, M., 2016e. Traceability of fluorescent engineered nanomaterials and their fate in complex liquid waste matrices. Environmental pollution (Barking, Essex : 1987) 214, 795-805.

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