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## **Mobility and Transformation of CdSe/ZnS Quantum Dots in Soil: Role of the Capping Ligands and Ageing Effect**

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1 **Mobility and Transformation of CdSe/ZnS Quantum Dots in Soil: Role of the Capping**  
2 **Ligands and Ageing Effect**

3

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21

22 Abstract

23

24 The increasing application of Quantum Dots (QDs) is cause of concern for the potential negative  
25 effects for the ecosystem, especially in soils that may act as a sink. In this study, soil leaching  
26 experiments were performed in quartz sand packed columns to investigate the behavior of core-shell  
27 CdSe/ZnS QDs coated with either small ligands (TGA-QDs) or more complex polymers (POAMA-QDs).  
28 Fluorescence emission was compared to mass spectrometric measurements to assess the  
29 nanoparticles (NPs) state in both the leachate (transported species) and porous media (deposited  
30 amounts). Although both QDs were strongly retained in the column, large differences were observed  
31 depending on their capping ligand stability. Specifically, for TGA-QDs elution was negligible and the  
32 retained fraction accumulated in the top-columns. Furthermore, 74% of the NPs were degraded and  
33 38% of the Se was found in the leachate in non-NPs state. Conversely, POAMA-QDs were recovered to  
34 a larger extent (78.1%), and displayed a higher transport along the soil profile. Further experiments  
35 with altered NPs showed that homo-aggregation of the QDs prior injection determined a reduced  
36 mobility but no significant changes in their stability. Eventually, ageing of the NPs in the column (15  
37 days) caused the disruption of up to 92% of the original QDs and the immobilization of NPs and  
38 metals. These results indicate that QDs will accumulate in top-soils, where transformations  
39 phenomena will determine the overall transport, persistency and degradation of these chemicals.  
40 Once accumulated, they may act as a source for potentially toxic Cd and Se metal species displaying  
41 enhanced mobility.

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45	<b>Keywords</b>
46	Nanoparticles
47	Quantum dots
48	Transformation
49	Mobility
50	Soil
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## 68 1. Introduction

69

70 Engineered nanoparticles (NPs) are currently incorporated in a large number of consumer products  
71 and their production is expected to increase dramatically in the next years (Roco 2011). Quantum  
72 Dots (QDs) are among the most promising materials in emerging nanotechnologies due to the unique  
73 high-yield and size-tunable electrical and optical properties (Bruchez et al., 1998, Bera et al., 2010),  
74 which make them ideal candidates for applications in photovoltaics and biomedical imaging as well as  
75 in the construction of sensors and electronics in general (Alivisatos 2004; Kamat 2008; Anikeeva et al.,  
76 2009; Kalita et al., 2016). Such properties are correlated to QDs distinctive structure where a semi-  
77 conductive metal core, usually composed of CdTe, CdSe or InP, is surrounded by a shell (e.g. ZnS,  
78 CdSe). The resulting core-shell nanocrystals have diameters in the 2-100 nm size range and are  
79 commonly functionalized with organic polymer coatings in order to increase their stability and  
80 solubility in aqueous media, i.e. their applicability (Dabbousi et al., 1997; Bruchez et al., 1998; Bera et  
81 al., 2010; Karakoti et al., 2015). There is concern for the possible negative effects arising from the  
82 wide usage of engineered nanomaterials and in the last two decades several countries and  
83 organizations (e.g. European Commission; US Environmental Protection Agency) have launched  
84 campaigns for the study of the associated risks for humans and the ecosystem (Dunphy et al., 2006.  
85 Owen et al., 2007; U.S. EPA, 2011; Oomen et al., 2018). In particular, QDs may display peculiar  
86 reactivity and persistency and their toxicity could be related to the NPs form, the release of  
87 potentially toxic metals and enhanced by the organic ligands (Hardman, 2006) as highlighted by  
88 recent works showing the noxious effects on bacteria and eukariota (e.g. Khare and Kumari, 2017).  
89 QDs release in the environment can occur from point and diffuse sources, such as the use and  
90 disposal of consumer and biomedical products but also the waste production and land application of

91 biosolids. Thus, soil may act as a sink for NPs accumulation and understanding their behavior in the  
92 terrestrial ecosystems is of utmost importance for risk assessment and management (Cornelis et al.,  
93 2014). However, most research on QDs fate in environmental systems has been focused on  
94 freshwater (Xiao et al., 2016) and the number of studies addressing their behavior in other  
95 compartments is still limited. Research has been conducted to investigate the deposition of QDs onto  
96 porous media employing quartz crystal microbalance (QCM; Quevedo & Tufenkij, 2009; Quevedo et  
97 al., 2013) and packed-bed soil column systems, with the latter being mostly applied. In general,  
98 although the comparison between these studies is complicated by the differences in experimental  
99 settings and materials utilized (e.g. soil matrices, NPs compositions and coatings), a high mobility of  
100 the QDs was observed at low ionic strength and neutral pH in unsaturated conditions representative  
101 of natural subsurface systems (Usuyur et al., 2010) as well as in saturated granular matrices consisting  
102 of either standardized porous media (e.g. quartz sand) or real soil samples (Torkzaban et al., 2010; Al-  
103 Salim et al., 2011). However, retention of the QDs during column experiments was greatly enhanced  
104 in presence of divalent cations, likely due to cation bridging between the negatively charged capping  
105 groups (Quevedo & Tufenkij, 2012; Torkzaban et al., 2013), and when the collector surface presented  
106 impurities or was coated with iron (Torkzaban et al., 2010). Wang et al., (2013) systematically studied  
107 the effect of ionic strength, pH and NPs coating on the transport of QDs and reported enhanced  
108 mobility at decreasing ionic strength and increasing pH as well as a diminished retention of the  
109 carboxylated compared to the non-ionic coated NPs. These works agreed that QDs coating will  
110 ultimately affect their behavior in the real terrestrial systems and that its interaction with the natural  
111 components will determine the stability and environmental fate of the NPs. However, alteration of  
112 the nanomaterials pristine state during the transport experiments was scarcely investigated and may  
113 include ligand desorption, oxidation and aggregation/precipitation of the QDs, which have been

114 reported in aqueous systems as a consequence of irradiation and depending on solution chemistry  
115 (Aldana et al., 2001; Zhang et al., 2008; Zhang et al., 2008b; Lead et al., 2018). In soil, Navarro et al.,  
116 (2011) found evidences of degradation during leaching studies in presence of organic matter and  
117 suggested that the stability of these chemicals over the long period is questionable whereas, more  
118 recently, Faucher et al. (2018) reported dissolution and aggregation of the QDs in soil solutions.  
119 However, the extent and kinetic of these phenomena remain unclear, especially regarding QDs  
120 dissolution, which may cause the release and mobilization of novel potentially toxic species such as  
121  $Cd^{2+}$ ,  $Se^{2-}$  and  $SeO_3^{2-}$ . Furthermore, such processes may be affected by QDs ageing and general  
122 alteration of their pristine state. For instance, increased toxicity was reported on Zebra Fish and  
123 bacteria as a consequence of QDs weathering (Mahendra et al., 2009; Wiecinski et al., 2013) whereas  
124 Torkzaban et al. (2013) found a diminished release of deposited QDs from the soil with increasing  
125 ageing time. However, to date most of the studies on QDs environmental fate were focused on  
126 pristine as-produced nanomaterials, which physico-chemical properties may be representative of the  
127 behavior occurring at manufacturing and processing sites but not upon release in the environment  
128 (Lowry et al., 2012). In this context, Mitrano and Nowack (2017) recently stressed the need for novel  
129 research focused on the transformation and ageing of nanoparticles, in order to better represent the  
130 real conditions at which they are found in the ecosystem and allow a more precise and life-cycle  
131 based assessment of these nanomaterials.

132 In this work we examined the mobility and stability of two QDs nanoparticles presenting nearly  
133 identical nanocrystalline structure but different organic coating. A series of soil leaching experiments  
134 were conducted to study the behavior of the two QDs in quartz sand, with regard to leached but also  
135 deposited amounts, which have often been neglected in literature. The comparison between  
136 fluorescence emission and mass spectrometric measurements allowed an estimation of NPs



137 transformation during the experiments whereas a further assessment of the NPs dissolution was  
138 provided by ultrafiltration of the leached samples. A second set of experiments was devoted to  
139 understanding the effect of NPs alteration and ageing on these processes. In particular, we  
140 investigated the effect of I) increased  $\text{Ca}^{2+}$ -mediated homo-aggregation of the QDs in the spiking  
141 solution and II) the ageing of the NPs in the column systems, i.e. their incubation in quartz sand for 15  
142 days prior the experiments. The main aim of this study is to provide observation of QDs behavior in  
143 simplified environmental systems, which can provide the basis for future works in more complex  
144 matrices. These results will help the understanding of nanomaterials behavior and fate in soils, with  
145 particular regard to small NPs such as QDs, as well as the effects of their transformation and ageing in  
146 environmental systems.

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## 149 2. Materials and Methods

150

### 151 2.1. Chemicals and Quantum Dots synthesis

152

153 The chemicals used for QDs nanocrystals and organic coating synthesis were purchased from Sigma  
154 Aldrich (unless specified) and used without further purification: sulfur (99.9%), cadmium oxide  
155 (99.9%), selenium (99.9%), anhydrous zinc acetate (99.9%), oleic acid (90%), trioctylphospine (90%), 1-  
156 octadecene (90%), chloroform (99%), thioglycolic acid (99%), poly(maleic anhydride-alt-1-octadecene)  
157 and ethanolamine (99%, Alfa Aesar). Concentrated nitric acid (65%) for samples acidification and  
158 digestion and hydrogen peroxide (30%) were purchased from VWR whereas ultra-pure milli-Q water  
159 (UPW) was produced in the laboratory with a Millipore purification system (Merck, Fontenay-sous-

160 Bois, France). The core-shell CdSe/ZnS QDs were synthesized in our group according to the single-step  
161 protocol reported by Bae et al., (2008) with minor modifications, i.e. the use of zinc oxide instead of  
162 zinc acetate as precursor. Purification of the QDs was achieved as following: first, the nanocrystals  
163 were dissolved in chloroform and isolated by precipitation after centrifugation at 6000 rpm for 10 min  
164 (5810 R centrifuge; Eppendorf Amburg, Germany). Then, the excess of reagents was removed with  
165 consecutive steps of centrifugation (6000 rpm, 10 min) and filtration (PTFE 0.2  $\mu$ m, Sigma Aldrich).  
166 After the synthesis, different batches of QDs nanocrystals were functionalized with organic polymers,  
167 in order to enhance their solubility in aqueous media. Two different coatings were selected based on  
168 synthesis reproducibility and yield. Specifically, the relatively simple thioglycolic acid, consisting of a  
169 short organic chain presenting both thiol and carboxylic acid functional groups (TGA, Zhu et al., 2014)  
170 was compared to the more complex organic polymer poly(maleic anhydride-alt-1-octadecene)  
171 (POAMA, Pellegrino et al., 2004). According to Faurier et al., (2017), the QDs are expected to have a  
172 CdS gradient between the CdSe core and the ZnS shell whereas the yellowish color and fluorescence  
173 emission in the green portion of the visible spectra indicated NPs diameter of 7 nm, with core size of  
174 circa 3.4 nm. The final QDs stock solutions in ultrapure water and at pH 11 were stored at 4C in the  
175 dark and a visual assessment of their homogeneity and limpidity was routinely performed with a  
176 BTCP-20.MC compact transilluminator (Vilber Lourmat, Collegien, France).

177

178

## 179 2.2. Soil leaching experiments

180

181 IOTA high purity quartz sand from Unimin Corporation (Le Sueur, MN, US) was used as the porous  
182 media for all the soil leaching experiments. Grain size observed with Scanning Electron Microscopy

183 coupled to Energy Dispersive X-Ray Analysis (SEM-EDX) ranged from 280 to 340  $\mu\text{m}$  ( $n=20$ ), with  
184 average grain diameter of 300  $\mu\text{m}$ . In order to remove metals and organic impurities from the quartz  
185 sand, a cleaning protocol was performed similar to what reported by Wang et al., (2010). Briefly, the  
186 sand was soaked in 10%  $\text{HNO}_3$  placed in an ultrasonic bath (Ultrasonic Cleaner, VWR) at 60 Hz for 30  
187 min and stirred every 5 min. The same procedure was repeated once with UPW, then once with 5%  
188  $\text{H}_2\text{O}_2$  and eventually twice with UPW. The whole wash/rinse protocol was carried out three times and  
189 the sand was eventually rinsed with 1 mM  $\text{Ca}(\text{NO}_3)_2$  until pH equilibration, then rinsed with UPW and  
190 oven dried at 65 C. The column apparatus consisted of custom-made 23 mL volume polycarbonate  
191 columns (internal diameter 2.3 cm, length 4 cm) equipped with 25 mm polycarbonate filter holders  
192 (Sartorius GbH, Goettingen, Germany) sealed with polytetrafluoroethylene (PTFE) seal tape to  
193 prevent leaking. Glass fiber filters (HA type; VWR) were placed at both extremities and approximately  
194 23 g of quartz sand were added to each column with 0.5 cm increments in wet-packing conditions. A  
195 background electrolyte, consisting of 1 mM  $\text{Ca}(\text{NO}_3)_2$  solution at pH 7 was flushed in bottom-up mode  
196 through the vertically oriented columns at a constant flow of 0.5 mL/min using a peristaltic pump  
197 (Minipuls3; Gilson, Middleton, WI, USA). The resulting pore-water velocity of 4.5 m/day is  
198 representative of typical coarse textured porous media and has been previously applied to study the  
199 transport of NPs in saturated column systems (Torkzaban et al., 2013). At these conditions, the  
200 porosity and pore volume (PV) were about 0.4 and 6.5 mL respectively, with PV residence time in the  
201 column of 13 min. Each soil leaching experiment was performed in duplicate and the columns were  
202 covered with aluminum foil to prevent exposure to light. The columns were first equilibrated with the  
203 background electrolyte solution for at least 24 hrs (circa 100 PV) before introducing 0.5 mL of QDs  
204 spiking solutions and 0.5 mL of a 120 mg/L  $\text{Br}^-$  tracer solution with the procedure reported by Navarro  
205 et al. (2011). A scheme of the experimental set-up is provided in the [supplementary info, fig. S1](#). 0.5

206 ml/min; 4.5 m/day). Spiking solution of the QDs in 1 mM Ca(NO<sub>3</sub>)<sub>2</sub> and pH 7.0 were obtained from  
207 dilutions of the stock solution for a concentration of 10.5 ± 0.1 µg/mL Cd. This corresponded to 8.5 ±  
208 1.5 × 10<sup>13</sup> particles/mL (14.1 ± 2.5 nM) based on a CdSe density of 5.82 g/cm<sup>3</sup> and assuming NPs  
209 spherical shape with diameter of 3.4 nm. For experiments with altered (aggregated) QDs, spiking  
210 solution was prepared in 100 mM Ca(NO<sub>3</sub>)<sub>2</sub> solution, stored at room temperature in the dark for 4 hrs  
211 and then ultrasonicated for 15 min before introduction. For ageing experiments the QDs spiking  
212 solution was applied into the column, the peristaltic pumps were stopped, the tubing blocked with  
213 clamps and the experiments re-started after 15 d of incubation. In each experiment, after  
214 introduction of the QDs, 7 PV of background electrolyte were run through the column and 2 mL  
215 eluent samples were collected into 5 mL polypropylene vials. This corresponded to a resolution of  
216 circa 3 samples per PV. At the end of the experiments, the columns were first frozen at -18 °C  
217 overnight and then the quartz sand was extracted and cut into thin sections of 0.3 to 0.5 mm thick.  
218 The sections were transferred into 10 mL glass vials and freeze-dried with a Alpha 1-4 LD plus freeze  
219 drier (Bioblock Scientific, Rungis Complexe, France) operating at approximately -56 °C and 0.035 mbar  
220 for 48 hours.

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222

223

### 224 2.3 Samples processing and analysis

225

226 In general, since fluorescence emission is peculiar of the QDs nanocrystals, at least with regard to the  
227 pristine nanoparticles and CdSe cores (Pereira et al., 2016), it was used for estimation of the  
228 nanoparticle species during the experiments. Total Cd and Se were measured before and after

229 ultrafiltration (3 KDa) in order to assess total and dissolved metals concentrations, respectively. In  
230 detail, the 2 mL column eluent samples underwent fluorescence emission analysis for estimation of  
231 the QDs concentration and metal determination to assess the total Cd and Se contents. For  
232 fluorescence analysis, 0.5 mL was transferred into 5 mL polypropylene tubes and diluted with 3.5 mL  
233 of 1 mM  $\text{Ca}(\text{NO}_3)_2$  at pH 7 then analyzed within 3 min from the collection to minimize alteration of the  
234 analytes (e.g. dissolution with consequent loss of fluorescence). For metal content analysis, 0.5 mL  
235 samples was transferred into 14 mL Falcon tubes, diluted up to 10 mL with UPW and acidified for a  
236 final 1%  $\text{HNO}_3$  concentration. Additional 0.5 mL sample underwent ultrafiltration with 3 KDa  
237 regenerated cellulose centrifugal filters (Amicon 4-ultra, Merck), operated with centrifugation at 4000  
238 rpm for 35 min. The filtrated samples were then diluted and acidified for Cd and Se analysis following  
239 a similar procedure than above. For time reasons, the ultrafiltration was carried twice during each  
240 experiment with sets of 9 samples each. The remaining amount was stored at 4°C in the dark.  
241 Extraction of the QDs from the lyophilized quartz sand sections was achieved with 15 min  
242 ultrasonication of 0.5 g samples in 4 mL of 50 mM NaCl solution at pH 10 at room temperature.  
243 Specifically,  $\text{Na}^+$  was employed to enhance the extraction of the deposited QDs via cation exchange  
244 onto the sand surface whereas the high pH prevented dissolution and aggregation/precipitation of  
245 the QDs in solution ([Torkzaban et al., 2013](#)). Recovery of extraction of the QDs from the quartz sand  
246 were  $78 \pm 3 \%$  and  $85 \pm 2 \%$  for TGA-QDs and POAMA-QDs, respectively. Acid digestion was carried  
247 out for the analysis of metals in the solid samples as following: first, 0.5 g of each sample was  
248 transferred into 50 mL falcon tubes and 3 ml of concentrated acid (1:1;  $\text{HNO}_3$ :UPW) were added  
249 before undergoing ultrasonication for 30 min at room temperature. Then, 2 mL of  $\text{H}_2\text{O}_2$  and 3 mL of  
250 UPW were added and the samples ultrasonicated again at the same conditions. Eventually, the  
251 samples were diluted 6 times with UPW for a final 2%  $\text{HNO}_3$  concentration. The recovery for Cd and

252 Se extraction from the quartz sand was  $96 \pm 3 \%$  and  $92 \pm 4 \%$ , respectively. Fluorescence emission  
253 analysis of both eluent and soil extracts samples were performed with a Horiba Scientific FluoroMax-4  
254 spectrofluorimeter, with excitation wavelength set at 310 nm and emission spectra recorded in the  
255 480-600 nm range. The measurements were repeated at least two times per samples and  
256 quantitation was achieved with external calibration lines obtained from dilutions of the QDs stock  
257 solutions at concentrations ranging from 1 to 500  $\mu\text{g/L}$  Cd (at least 6 points). Limit of quantitation for  
258 the QDs, based on Cd concentration, was 0.3  $\mu\text{g/L}$  (equivalent to  $2.1\text{E}+9$  particles/mL). The metal  
259 content in the samples was analysed with a sector field inductively coupled plasma mass  
260 spectrometer (SF-ICP-MS, Element II, ThermoScientific, Bremen, Germany). Measurements of Se and  
261 Cd were carried out in high and low resolution modes, respectively. Quantitation was achieved  
262 analyzing standard solution at known concentrations of the elements ranging from 1 ng/L to 10  $\mu\text{g/L}$   
263 ( $n=5$ ) and Indium at the concentration of 1  $\mu\text{g/L}$  was continuously introduced during each analysis as  
264 internal standard. Limit of detection and quantitation were in the 100 ng/L and 10 ng/L ranges for Se  
265 and Cd, respectively. The data were processed with uFreasi software (Tharaud et al., 2015). Analysis  
266 of the metals digested from the quartz sand were done with an ICP-OES ICAP 6000 Series  
267 (ThermoScientific) equipped with an ASX-520 autosampler (Cetac, Omaha, NE, USA). Bromide  
268 tracer analysis were performed with a Dionex ICS 1100 ion chromatography system equipped  
269 with AS DV autosampler (ThermoScientific).

270

271

## 272 3. Results and discussion

### 273 3.1. Mobility and Transformation of QDs

274

275 The synthesized NPs presented very similar CdSe/ZnS core-shell structures, with Zn/Cd ratio of 2.8  
276 and 3.0, and Zn/Se ratio of 7.8 and 8.7, for TGA-QDs and POAMA-QDs, respectively. Furthermore, the  
277 QDs displayed similar fluorescence spectra in the green portion of the visible spectrum (500- 600 nm),  
278 with maximum yield at excitation wavelength of 310 nm and emission centered at 551 nm and 534  
279 nm for TGA-QDs and POAMA-QDs, respectively ([supplementary info, fig. S2](#)). Thus, the main  
280 difference between the two NPs under investigation consisted in the ligand covalently attached to the  
281 surface, with TGA being a short organic chain and POAMA a more complex aromatic polymer  
282 ([supplementary info, fig. S3 and S4](#)). In this work, the fluorescence measurements were considered as  
283 indicative of a nanoparticles state, since the loss of emission is expected to correspond to a severe  
284 alteration of their core-shell structure (e.g. total dissolution). It must be noted that these could not  
285 necessarily discern between pristine and slightly altered nanomaterials (e.g. following partial  
286 dissolution of the ZnS shell). Fluorescence was compared with the ICP-MS measurements, which  
287 provided a quantitative assessment of the QDs metals but no information about their state (e.g. NPs  
288 or free ions). The mass balances for each experiment are provided in supplementary information  
289 ([Table S5](#)). Since Zn mass balances were generally >120% at the end of the experiments, Zn was not  
290 considered for further evaluation. Higher Zn concentrations may be due to background levels in the  
291 porous media or eluent solutions as well as incidental introduction during samples treatment. Thus,  
292 the results presented here are focused on Cd and Se analysis, which seemed not affected by Zn  
293 imbalances and presented recoveries generally > 90%.

294

295

296

297 The first aim of the present work was to study the QDs mobility during soil leaching experiments and  
298 to provide an assessment of their behavior and transformation. Figure 1 shows the breakthrough  
299 curves (BTC) obtained for POAMA-QDs (Fig. 1a) and TGA-QDs (Fig. 1b) in which NPs in the leachate  
300 (fluorescence, black lines) are shown together with Cd (red) and Se (green). Similar to what was  
301 reported by Al-Salim et al. (2011) during column studies in silt loam top-soil systems, the QDs were  
302 eluted after 1 PV at the beginning of the experiments and displayed little or no significant difference  
303 in the physical transport when compared to the conservative Br-tracer ([supplementary info, fig. S6](#)).  
304 However, ICP-MS analysis revealed that different processes occurred during the transport due to  
305 differences between the NPs in the capping ligand stability. Specifically, POAMA-QDs (fig. 1a) metals  
306 BTCs were well correlated and displayed no significant difference with the measured fluorescence,  
307 suggesting that Cd and Se were transported as clusters and that QDs leached from the columns in a  
308 nanoparticulated form, at least with regard to the CdSe inner core liable for fluorescence emission.  
309 The core integrity was further confirmed by the absence or low concentrations of Cd and Se after  
310 samples ultrafiltration (Fig. 1a, light lines), which is selective for the QDs and generally for particles  
311 larger than 3 KDa. Cd traces (in ultrafiltrates) were also measured immediately at the starting of the  
312 experiment and likely belonged to endogenous Cd, which eluted from the column before QDs. In  
313 contrast, TGA-QDs were slightly more retained in the column, with elution starting after 1.3 PV, and a  
314 significant difference between NPs and metals BTC was observed (fig. 1b). Indeed, while QDs  
315 concentrations were negligible, almost 40% of total Se and 0.5% of Cd were recovered in the leachate.  
316 This indicates that QDs transformation occurred during the experiment, resulting in the release of  
317 dissolved metal species, which transport was enhanced in comparison with the nanoparticulate  
318 forms. Also, since Se is confined into the inner portion of the QDs core-shell structure, its large  
319 concentration in the leachate necessarily implies at least a partial removal of both the ZnS shell and



320 organic coating outer layers. In general, such degradation is cause of concern for mobilization of  
321 potentially toxic elements from NPs, including Cd(II), Se(-II), Se(IV) and several reactive oxygen species  
322 (ROS) (Yaghini et al., 2014). In this context, the larger amount of Se in the leachate can be explained  
323 assuming the formation of novel oxyanions Se species (such as  $\text{SeO}_3^{2-}$ ), similar to those reported by  
324 Navarro et al., (2011) during soil leaching studies, and considering the electrostatic repulsion with the  
325 negatively charged quartz sand. Accordingly, Cd divalent cation retention is in agreement with its fast  
326 sorption kinetic to soil. However, no Cd and only half of eluted Se were present in the samples after  
327 ultrafiltration (fig. 1b, light lines). Since the low fluorescence measured in the non-filtered leachate  
328 precluded the presence of large amounts of intact CdSe cores, the Se retention observed suggests the  
329 formation of colloidal metal phases withheld in the 3 KDa membrane. Interestingly, colloidal Se  
330 species (such as hydrogen selenide ion  $\text{HSe}^-$  and colloidal elemental selenium) were reported to  
331 catalyze aerobic oxidation of thiols (Nuttal and Allen, 1984) and it could be expected that their  
332 released after a first dissolution of the TGA-QDs, may have further enhanced the ligand  
333 transformation, leading to the extensive degradation observed. In general, although the original  
334 assumption was of non-favorable deposition conditions, with minimal retention due to the  
335 electrostatic repulsion between NPs and quartz sand, both QDs displayed a strong retentive behavior  
336 and leached fractions were 2.1% and 0.1% only of the POAMA-QDs and TGA-QDs initial amounts,  
337 respectively. Torkzaban et al., (2013) reported deposition of 94% of the acrylic-capped CdTe QDs,  
338 which is similar to the Cd and Se POAMA-QDs deposition in this study (~93%), suggesting that  
339 enhanced NPs retention was due to the presence of divalent cations in solution (2 mM  $\text{CaCl}_2$ ). In  
340 detail,  $\text{Ca}^{2+}$ -mediated deposition can be explained with the compression of the electrical double layer  
341 onto the NPs surface, which in turn determined a decreased repulsion between NPs and mineral  
342 surface. Furthermore, enhanced deposition of the QDs could result from the formation of homo-

343 aggregates due to both the diminished mutual repulsion between NPs and the capacity of multivalent  
344 cations to complex the NPs by bridging the negatively charged capping groups (Quevedo and Tufenkji,  
345 2011; Torkzaban et al., 2013).

346

347 In fig. 2, soil profiles were plotted to show the retained QDs and metals distribution along the  
348 columns. With regard to the POAMA-QDs (fig. 2a), although 77% of the deposited NPs was found in  
349 the first 0.5 cm, gradually decreasing amounts in the further sections revealed that the QDs migrated  
350 along the soil profile. Similarly, the larger fractions of Cd (71%) and Se (57%) were retained in the top  
351 column with smaller concentrations detected in the further sections. The correlation between metals  
352 and QDs distributions suggested that most of the NPs were intact during migration, confirming the  
353 overall stability previously observed in the leachate. Despite this the NPs quantified on the basis of  
354 fluorescence emission, which is indicative of pristine structures and/or CdSe cores (Pereira et al.,  
355 2016) accounted for 76% of the initial amount, showing that also a portion of the POAMA-QDs were  
356 altered after or during deposition. This observation is further supported by the minor differences  
357 between Cd and Se concentrations in the column segments, with the latter moving deeper along the  
358 profile. As expected from the analysis of the leachate, such phenomena had a larger extent in TGA-  
359 QDs amended column (fig. 2b). Indeed, although the quasi totality of Cd and 55% of Se were  
360 recovered in the quartz sand, according with the amounts measured in the eluent, only 25.9% of  
361 these corresponded to pristine QDs. Furthermore, while Cd and Se had a distribution similar to that of  
362 POAMA-QDs, with >65% of the metals in the top-column and the rest distributed in the further  
363 sections, the NPs displayed no migration and were entirely (> 95%) accumulated in the first 0.5 cm.  
364 The concentration of Se and QDs in this section were similar and within the measured error,  
365 indicating that Se was retained in the top column as NPs and that transport occurred only for the

366 species resulting from NPs degradation. Thus, it can be assumed that in addition to exposing the core-  
367 shell nanocrystals to the outer environment, with consequent dissolution phenomena, the ligand  
368 removal also caused the immobilization of the QDs onto the porous media due to the loss of surface  
369 coatings negative charges and non-favorable deposition conditions. It must be noted that the  
370 instability of thiol-capped QDs, similar to those in this work, was investigated by previous studies in  
371 aqueous media, which reported a pH-dependent aggregation and capping desorption of the NPs as  
372 well as light-mediated oxidation with consequent precipitation of the nanocrystals (Aldana et al.,  
373 2001; Zhang et al., 2008b). However, the same works highlighted the relative stability of QDs  
374 (homogeneous dispersion and no precipitation) at the experimental conditions we applied (neutral  
375 pH, no light exposure) suggesting that degradation during the leaching experiments was enhanced by  
376 their interaction with the quartz sand matrix. Nonetheless, similar transformation phenomena were  
377 often neglected during soil transport studies, given the assumption that QDs were stable in soil  
378 matrices and during the relatively short duration of typical column experiments (usually 1-3 hrs) (e.g.  
379 Wang et al., 2013), and evidences of QDs degradation were only reported after long-term exposure of  
380 NPs in soil systems (Navarro et al., 2011). Rather, we observed that a fast ligand desorption may occur  
381 in soil with consequent transformation of the nanomaterials in the short-term. In this context, similar  
382 processes may hinder both the qualitative (speciation) and quantitative (deposition, attachment  
383 efficiency) assessment of QDs fate. For instance, in the case of TGA-QDs in this study the analysis of  
384 QDs fluorescence only may lead to an overestimation of deposited amounts, whereas mass  
385 spectrometric measurements alone would result in the overestimation of the eluted QDs.

386

387

388 3.2 Effect of Ageing and Alteration of the QDs

389

390 Once released in the environment, NPs will undergo modification of their state and properties due to  
391 the interactions with the natural components and ageing in the natural media ([Mitrano and Novak,](#)  
392 [2017](#)). Thus, a second set of soil leaching studies was carried out to investigate the effect that  
393 alteration of the pristine QDs may have on their behavior during their transport in soil.

394

395

396 In the first ageing experiment, POAMA-QDs spiking solution was prepared at a larger concentration of  
397  $\text{Ca}^{2+}$  and incubated in the dark for a few hours before being introduced in the column. As shown in fig.  
398 3a, this resulted in a higher QDs sorption onto quartz sand, and their complete retention in the  
399 column, i.e. no fluorescence measured in the leachate. A fraction of Cd and Se ( $0.5\pm 0.1\%$  and  $6.9\pm$   
400  $2.4\%$ ; respectively) eluted at the beginning of the experiment with leaching profiles similar to those  
401 of the pristine QDs (Fig. 1a). However, no significant difference was observed with the concentrations  
402 found after ultrafiltration of the samples, suggesting that these were free metal species formed either  
403 in the preparation and ageing of the spiking solution or during NPs transport in the column.

404 Homo- and hetero-aggregation of nanomaterials are important processes driving their environmental  
405 fate and effects (Lead et al., 2018) and their characterization (e.g. kinetics of aggregation,  
406 determination of attachment efficiency) is increasingly being used for predicting NPs behavior and  
407 transport models (Geitner et al., 2017). Increasing ionic strength of multivalent cations in solution is  
408 known to cause increasing hydrodynamic diameters and reduced electrophoretic mobility of QDs  
409 ([Wang et al., 2013](#); [Quevedo and Tufenkji, 2011](#)). For instance, Quevedo and Tufenkji (2011) reported  
410 up to 15-fold increase of CdSe QDs diameter (assessed by transmission electron microscopy, TEM) at  
411  $\text{Ca}^{2+}$  concentrations similar to those applied in the present study (2,5 mM). In this case, the

412 hydrodynamic diameter of QDs, measured by dynamic light scattering (DLS) was circa 550 nm and  
413 resulted in enhanced retention and one order of magnitude increase in the attachment efficiency.  
414 Although such measurements were not performed here, recent studies by some of the authors of this  
415 work showed aggregation of POAMA-QDs in aqueous suspensions and soil solutions (Faucher et al.,  
416 2018). Thus, it can be assumed that homo-aggregation of the NPs prior introduction in the columns  
417 imposed a reduced transport due to the larger size and smaller charge density of QDs. This also  
418 resulted in a decreased mobility along the soil profile (fig. 2c), with 95% of the retained NPs  
419 accumulated in the top-columns together with the largest fractions of Cd and Se. The metals were  
420 recovered to a larger extent, specifically 94% and 97% for Cd and Se, respectively (SI, table S4).  
421 Furthermore, in the quartz sand, 80% of the metals were found in NPs form, indicating the relative  
422 stability of the altered NPs, likely due to the decreasing of the surface to volume ratio in the  
423 aggregates, i.e. a smaller surface exposed to the outer environment. Based on these results, it can be  
424 expected that aggregation will determine an even more limited mobility and higher persistency of  
425 QDs in terrestrial systems. However, it must be noted that the present work investigated the effect of  
426 homo-aggregation processes, which may only be representative of specific environmental scenarios  
427 where the presence of high concentrations are expected (e.g. disposal of consumer products, hot-  
428 spots of contaminations) and that future works will need to clarify the effect of hetero-aggregation  
429 phenomena (e.g. interaction with organic matter), which are generally considered more relevant after  
430 dispersion of engineered nanomaterials in real ecosystems.

431 In the final set of experiments, NPs were aged in contact with the quartz sand before leaching in order  
432 to determine changes in their behaviour and mobility over time. Thus, the experiments were carried  
433 out at the same experimental conditions as previously (see section 3.1), but elution started 15 days  
434 after the introduction of QDs in the columns. The incubation time of 15 days was chosen in order to

435 represent short to medium ageing periods and was previously applied in environmental fate studies  
436 (Navarro et al., 2011). In general, ageing resulted in a reduced NPs transport in comparison to the  
437 non-aged experiments, with neither of the two QDs types leaching from the columns (fig.3b and 3c,  
438 black lines), and with retained fractions being almost totally (98%) accumulated in the first section of  
439 the soil profile (fig. 2d and 2e, fluorescence bars). This behavior can be explained by an enhanced  
440 time-dependent NPs sorption to the quartz sand, as well as the consequence of homo-aggregation  
441 induced by the presence of a high NPs concentration in the top column for a relatively long period.  
442 Navarro et al., (2011) reported increased mobility of thiol coated CdSe QDs after ageing in soil  
443 matrices due to the presence of organic matter in the system (i.e. ethylenediaminetetraacetic acid in  
444 the eluent and native organic acids in the soil). Furthermore, the authors found evidences of NPs  
445 degradation over time and suggested that organic material acted as chelating agent for the metals  
446 species originated from the QDs. In this study, both QDs were transformed to a large extent but in the  
447 absence of organic matter the etching of the pristine structures (e.g. transformation/desorption of  
448 the capping ligands) likely contributed at enhancing their deposition onto the sand. Indeed, the  
449 overall recovery from the system was only 22 +/- 5 % of the original POAMA-QDs (fig. 3b) and 8 +/- 2  
450 % for TGA-QDs. Notably, while a larger degradation of the latter was expected due to its lower  
451 stability (see section 3.1), severe transformation were also observed for POAMA-QDs, which instead  
452 remained almost intact in the non-aged experiments. Accordingly, the metal species resulting from  
453 NPs dissolution were more abundant in TGA-QDs leachate, and predominantly consisted of Se, due to  
454 preferential Cd sorption to the sand. As shown in fig. 3b and 3c, the ageing also caused significant  
455 changes leaching profiles of the metals, which eluted immediately at the beginning of the  
456 experiments, probably because of Cd and Se species migration in the saturated system during the  
457 incubation time. Interestingly, the overall larger degradation observed in the aged columns did not

458 result in a faster transport of metals in the liquid phase. Indeed, Se amounts in the leachate were  
459 lower than those found in the non-aged experiments and specifically 2.9 +/-0.6 % and 13.6 +/- 5.2 %  
460 for POAMA-QDs (fig. 3b) and TGA-QDs (fig. 3c), respectively. However, similar concentrations were  
461 found after ultrafiltration, specifically 2.4 +/- 0.1 for POAMA-QDs and 11.1 +/- 4.5, for TGA-QDs,  
462 suggesting that only free metal ions (e.g.  $\text{SeO}_3^{2-}$ ) were transported and that the metal colloids  
463 previously observed in the TGA-QDs non-aged column leachate (see fig. 1b) were deposited onto the  
464 quartz sand. Consequently, the amount of Se retained in the columns increased significantly from 54%  
465 of the non-aged experiments to 79% in aged TGA-QDs experiments. Analysis of the soil column  
466 profiles (fig. 2d and 2e) confirmed that Cd and Se did not consistently move as a cluster in the quartz  
467 sand confirming the disruption of the NPs form. Specifically, in both studies more than 90% of Cd was  
468 accumulated in the first 0.5 cm whereas Se was detected throughout the soil column profiles, with  
469 larger migration in TGA-QDs columns where >50% of Se migrated from the introduction spot to  
470 further segments. Nonetheless, fluorescence emission recorded in the top column sections extracts  
471 showed the presence of potentially intact CdSe QDs cores deposited. However, analysis of the spectra  
472 revealed that an 11 nm blue-shift was present in the emission maximum of the TGA-QDs whereas  
473 POAMA-QDs spectra had a 4 nm shift to the right ([supplementary info, fig. S7 and S8](#)). Interestingly,  
474 similar red-shift was also recorded for QDs recovered from the columns amended with altered spiking  
475 solution, i.e. where homo-aggregation was enhanced. Since QDs emission is correlated to their size,  
476 with emission wavelengths decreasing with the NPs diameters, these results suggest that the CdSe  
477 cores of TGA-QDs were partially altered and became smaller with ageing. On the contrary, deposited  
478 POAMA-QDs cores were likely intact also due to aggregation phenomena that enhanced the sorption  
479 onto the sand and prevented dissolution of the structure. Eventually, the results of the ageing  
480 experiments showed that QDs will undergo profound alteration in the soil over time independently of

481 their synthetic route (i.e. the organic coating), but that the capping ligand will still determine the  
482 kinetic at which these transformations will occur.

483

#### 484 4. Conclusions

485

486 The transport of core-shell CdSe/ZnS QDs in quartz sand appeared to be limited at all conditions  
487 tested: pristine, altered and aged NPs. However, it must be noted that the soil column systems  
488 presented here were necessarily simplistic in comparison to real environmental systems, with regard  
489 to porous media and eluent compositions. These factors will play a major role in determining NPs fate  
490 in soils (Geitner et al., 2020) and experiments employing more complex matrices (e.g. in the presence  
491 of minerals and organic matter) are currently being performed in our team. The results presented  
492 suggest that QDs will be accumulated in surface soils upon release in the environment but dissolution  
493 occurring due to the alteration of the pristine structures (i.e. capping ligand desorption) will result in  
494 the formation of novel potentially toxic metal species, which mobility was enhanced in our  
495 experiments in comparison with intact NPs. Thus, the stability of the organic coatings-NPs complexes  
496 will be as important as their physico-chemical properties in dictating the eventual fate of QDs in soil  
497 matrices, with regard to both their speciation and partitioning. In particular, small capping ligands  
498 used in this study (e.g. thioglycolic acid, TGA) displayed faster desorption rates from the NPs surface,  
499 resulting in the immobilization of the nanocrystals onto the sand. The organic coating removal likely  
500 enhanced the exposure of ZnS shells and subsequently CdSe cores to the outer environment, resulting  
501 in a larger degradation of the NPs. On the contrary, the stability conferred by larger organic coatings,  
502 as the poly(maleic anhydride-alt-1-octadecene) (POAMA), will likely determine higher transport and  
503 accumulation of the pristine QDs. Although alteration of the NPs manufactured state, such as homo-



504 aggregation, may prevent degradation and enhance their persistency, we observed severe NPs  
505 transformation over time independently of their surface ligand. It must be noted that although the  
506 characterization of as-produced NPs is fundamental for the understanding of their environmental  
507 behavior, most nanomaterials are currently being incorporated in a variety of matrices, in the case of  
508 QDs electronics and optics. Hence, future works will need to investigate the release of these  
509 nanomaterials in the presence of (embedded) matrices in order to represent more realistic  
510 release/mobility pathways and contamination scenarios (Nowack et al., 2016).

511 The results presented here suggest that the stability of the QDs in soils is questionable during both  
512 the short- and long-term periods and that transformation phenomena will eventually determine the  
513 removal of these nanomaterials from the soil compartments. Furthermore, degradation phenomena  
514 may hinder a proper estimation and assessment of the QDs during transport and fate experiments,  
515 and future works will need to address such issues. In this context, the use of multiple techniques has  
516 been often recommended for the NPs characterization in environmental media in order to gather  
517 information about their state (e.g. pristine, aggregated, dissolved). In this work, the comparison of  
518 mass spectrometry and fluorescence analysis as well as the use of ultrafiltration proved to be valuable  
519 tools in discerning the NPs forms among the metal species detected. Similar strategies were recently  
520 applied by our team to determine quantum dots at low concentrations and in complex biological and  
521 environmental matrices (Supiandi et al., 2019; 2020). Nonetheless, future works will need to provide  
522 more qualitative information about the QDs speciation and to describe the occurrence of the  
523 degradation products in real soil media and their interaction with natural components.

524

525

526

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## Figure captions

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### Figure 1

Figure 1. a) POAMA QDs breakthrough curves (BTC) of Se (green), Cd (red) and fluorescence (black) reported as fractions (%) of the initial amount introduced in the columns. The darker and lighter lines represent the total fraction eluted before and after ultrafiltration, respectively. b), BTC obtained for TGA-QDs. Due to the large gap between Cd and Se concentrations, Se values refer to Y axis on the right.

### Figure 2

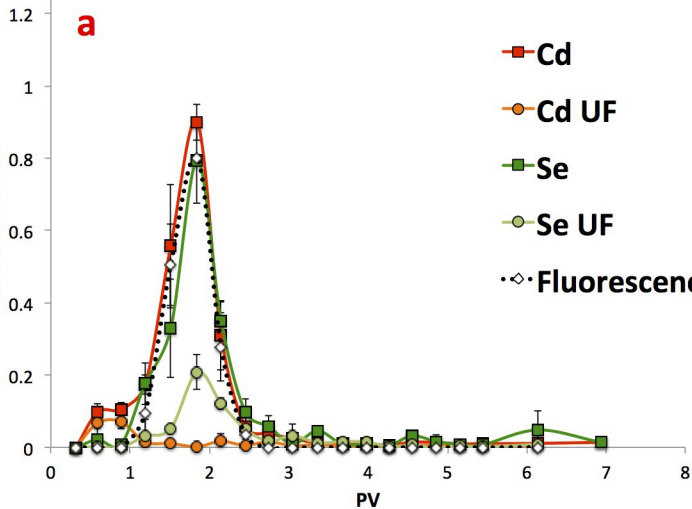
Figure 2. Soil column profiles obtained from analysis of the quartz sand after the leaching experiments. On top: a) POAMA-QDs, b) TGA-QDs. Bottom: c) aggregated POAMA-QDs solution, d) aged POAMA-QDs and e) aged TGA-QDs. Cd, Se, and NPs (fluorescence) are expressed as fraction of the initial amounts and each bar graph represent the percentage found in different sections of the columns.

### Figure 3

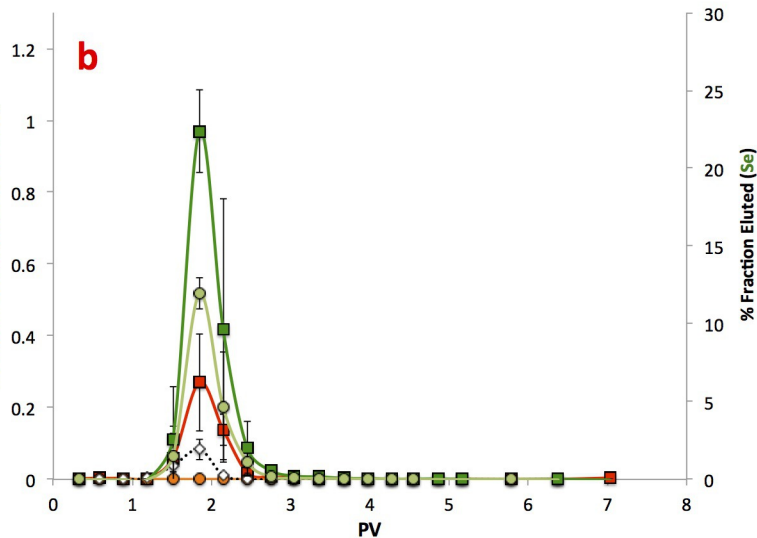
Figure 3. Breakthrough curves of the QDs during ageing experiments. a) altered POAMA-QDs b) aged POAMA-QDs and c) aged TGA-QDs. The darker and lighter lines for Se (green) and Cd (red) represent the fraction eluted (%) before and after ultrafiltration, respectively. No fluorescence (black lines) was observed in any of the samples.

**a**

% fraction eluted

**b**

% Fraction Eluted (Cd, fluorescence)



% Fraction Eluted (Se)

