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1 Estuary-on-a-chip: unexpected results for nanoparticles fate and 2 transport

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8

13 Abstract

14 The aim of this work is to evaluate the influence of a spatial salinity gradient, as encountered
15 in an estuarine when fresh water meets salty one, on the aggregation features of fullerene
16 nanoparticles aggregates (nC₆₀). To model these environmental conditions, we design a
17 specific microfluidic device. In literature, physical phenomena occurring in estuarine area,
18 such as the salinity gradient and the flow conditions, were never considered. Our results
19 suggest that even a short time exposure (couple of seconds) to a salinity gradient, i.e.
20 dynamical spatial conditions, profoundly affects the aggregation properties of nanoparticles
21 and therefore their environmental behavior and fate. It appears that a salinity gradient could
22 enhanced the stability of nanoparticles, especially at high ionic strength (closed to the
23 seawater level one). Contrary to the common approach of particle aggregation in the lab in
24 environmental conditions, our study shows the need to reconsider the spatial and temporal
25 variation of abiotic parameters (ionic strength, pH, organic matter concentration) in the
26 understanding and the evaluation of nanoparticles environmental fate and transportation
27 mechanisms.

28

29 **Keywords:** nanoparticles, fate, estuary, aggregation, microfluidic, lab-on-a-chip

1 **Introduction**

2 Because the main route of contaminant transport is river, estuarine systems are one of the
3 most targeted environmental compartment. Those ones are known to play a decisive role in
4 the conditioning of the colloidal materials life cycle^{1,2}. Estuarine systems are characterized by
5 specific physical and chemical conditions: salinity gradient, wastewater income, organic
6 matter, and human pressure (industrial and agricultural activities). From all these parameters
7 the ionic strength, characterized by the salinity, and the organic matter are the main
8 parameters that affect the stability of micro-nanoscale materials^{1,3}.

9 Over the last ten years, the influence of the ionic strength (IS) on the physical and chemical
10 properties of nanoparticles is one of the most studied parameter, for both carbon-based
11 (fullerene, carbon nanotubes)⁴⁻⁹ and metal-based (Ag, Au, TiO₂) nanomaterials¹⁰⁻¹⁴. To do so,
12 the kinetic of nanoparticles aggregation is generally determined by monitoring their size
13 evolution according to the time after an addition of a known concentration of electrolyte in
14 the bulk. However, since this measurement is made while the bulk salt concentration is
15 supposed to be homogeneous, it cannot be representative to what happens in the natural
16 environment. Indeed, these experiments are performed in static or large scale dynamic
17 reactors (such as columns) that are not representative of the natural conditions in which there
18 are spatial and temporal variations of the salt concentration. Indeed, the major issue in the
19 environmental media studies (in bulk liquid and porous media) is the limited applicability to
20 the real dynamic process affecting the transport of particles at environmental scale. More
21 generally NPs behaviors in the environment results from various physical and chemical
22 heterogeneities that the NPs come across. For estuarine system, the salinity gradient is one of
23 these spatial and temporal heterogeneities, and up to now nobody has considered its influence
24 on the fate of NPs.

1 Recently, new experimental methods and capacities, based on microfluidic devices, are
2 opening the door to environmental science for better understand the fate of species in dynamic
3 systems, closer to real natural conditions¹⁵⁻¹⁸. The aim of this work is to evaluate the fate of
4 nanoparticles, using fullerene aggregates (nC₆₀), in a salinity gradient. To do that we
5 developed a specific microfluidic device to simulate an environmentally representative
6 salinity gradient. Our results, compared to classical batch experiments, demonstrates a
7 different and specific aggregation kinetics, which raise new questions and concerns of the
8 existing knowledge on the environmental fate of nanoparticles in estuarine system.

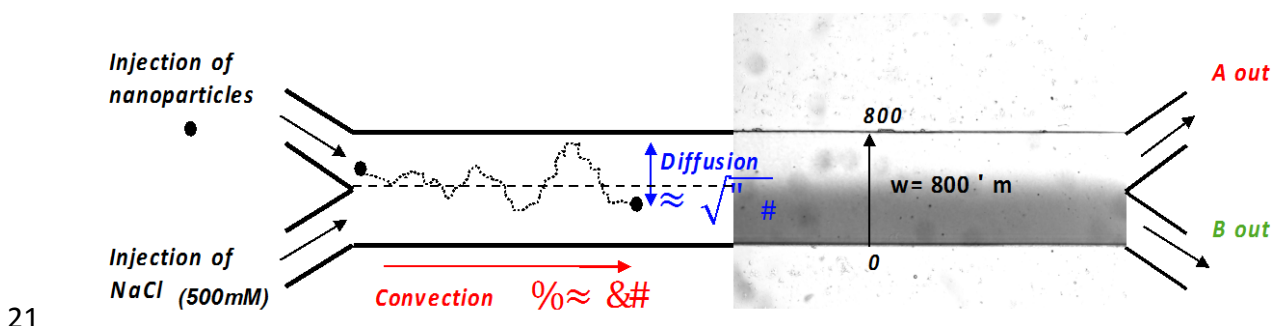
9 10 **Experimental**

11 12 *Sample preparation*

13 nC₆₀ were prepared according to classical procedure previously described¹⁹⁻²¹. Typically, 80
14 mg of C₆₀ powder (VWR, Fontenay-sous-Bois) were placed in an Erlenmeyer flask with 200
15 mL of deionized (DI) water (18.2 MΩ.cm at 25°C) and continuously stirred for 2 weeks.
16 Finally, the final fullerene aggregates solution (nC₆₀) was filtered at 0.45 μm to remove large
17 aggregates. The final concentration of nC₆₀ is 7.2±0.7 μg g⁻¹ and was characterized by both
18 Total Organic Carbon analyzer (Shimadzu, TOC-Vcph) and UV-Vis (Perkin Elmer
19 spectrophotometer, Lambda 650). The corresponding size distribution of the nC₆₀ initial stock
20 solution is d_{zH}=180.7 nm (with a polydispersity index, PDI=0.07) and is determined by in-situ
21 dynamic light scattering (Vasco-Flex, Cordouan Technologies, France). Preparation of nC₆₀
22 solutions were replicated 8 times with similar size distribution (see Electronic Supplemental
23 Information, Fig. S1).

24 25 *Microfluidic reactor design and operation*

1 We design a microfluidic device to simulate the estuarine salinity gradient (figure 1). We used
 2 standard soft lithography to make this microfluidic channel²². First we used a negative
 3 photoresist resin (Su8 2050 Microchem) that was spin coated on a silicon wafer, heated and
 4 cured with UV light through a mask on which the outline of the channel is printed. The resin
 5 is again heated and developed in a bath of PGMEA to remove the uncured part of the resin.
 6 Thereafter we cast polydimethylsiloxane (PDMS, Sylgard 184 silicone elastomer kit, Dow
 7 Corning) on the SU8 master. Once cured at 70°C for an hour the PDMS slab becomes solid, it
 8 is removed from the mold and punched to get the inlets and outlets holes of our channel. Then
 9 the channel is sealed by gluing the slab on a glass plate using a plasma cleaner (Harrick
 10 Plasma). This process renders the surface of the PDMS channel hydrophilic. To recover a
 11 hydrophobic surface we put the microfluidic device in an oven at 120°C for two hours. We
 12 inject fluid in the channel thanks to syringe pumps (KDS) at the inlets. In a typical
 13 experiment, we first saturate the channel with pure water and then connect pure water or salty
 14 on one inlet and a dilute fullerenes suspension on the other. The flow rates were controlled by
 15 syringe pump from 0.1 to 1.0 ml/h. At those rates the channel is filled in less than a couple of
 16 seconds.
 17 The microfluidic device is composed of 5 mm long and 200 μm wide inlets and outlets (“A
 18 out” and “B out”) arms on either side of a 3cm long channel with a width of 800 μm and a
 19 height of 75 μm (figure 1). In the following we focus on a given flow rate equals to 1.0 ml/h
 20 but we get similar results over a wide range of flow rates (0.1 to 1.0 ml/h).



1 *Figure 1: Scheme of the microfluidic dynamic and operation. At the entrance of the MD, two inlets are dedicated for the*
2 *injection of nC₆₀ (nanoparticles) in DI water and for the NaCl with salinity closed to Estuary mouth (500 mM). Two outlets*
3 *are identified, Aout and Bout, and are symmetric to the two entrances in term of geometry.*

4 The Figure 1 illustrate the microfluidic device used to simulate the estuarine salinity gradient.

5 Each microfluidic experiment are performed in three steps:

6 1-*Salt calibration.* We first inject pure water and a salty blue dye solution (Patent Blue from
7 Sigma Aldrich, #198218). This configuration allows us to visualize the salinity gradient on
8 the image that can be analyzed (Fig. S2 top). We checked that the dye does not affect the
9 salinity gradient. The average salt concentration at the two outlets were determined thanks to
10 the UV-spectra of the NaCl stock solution for various salt concentration (Fig. S2 middle and
11 bottom). To this end we collect samples at both outlets during one hour and then we
12 determine absorbance spectrum of the salty solutions.

13 2-*Diffusion nC₆₀ in the MD.* We inject, at a flow rate of 1 ml/h, nC₆₀ dispersed in water in one
14 arm and pure water in the other. We collect samples at the two outlets during one hour, we
15 stop the flow and then we determine the size distribution of the NPs. We found the same
16 distribution for both outlets (Fig. S3). This check step confirms that nC₆₀ diffuse around as it
17 flows through the microchip, i.e, the particle concentration is symmetric with respect to the
18 middle vertical plane of the straight channel.

19 3- *nC₆₀ aggregates in the salinity gradient.* We inject at a flow rate of 1 ml/h in each inlet
20 arm respectively dilute suspension of nC₆₀ in DI water and a salty dye solution (patent blue
21 dissolved in 500 mM of NaCl), a salinity that is encountered in the vicinity of Estuary mouths
22 ($\sim 30 \text{ g L}^{-1}$). In this experiment the average NaCl concentration is 42 mmol L^{-1} and 427 mmol
23 L^{-1} for A and B outlets, respectively. The residence time of the nC₆₀ in the salinity gradient is
24 lower than 3s in average. Again, after one hour of sample collection at the two outlets the
25 flow rate was stopped and we start measuring the temporal evolution of the nC₆₀ size
26 distribution at the two outlets for two hours. Thereafter we compare the temporal evolution of
27 the size distribution of the nC₆₀ aggregates with that of a batch experiment as described in

1 literature, i.e. dropwise concentrated NaCl dispersed into a nC₆₀ solution and then manually
2 stirred. All the experiments were replicated five times using for each replicate a new nC₆₀
3 stock solution and NaCl preparation.

4 5 *Size characterization by Dynamic Light Scattering*

6 We performed dynamic light scattering measurements within the collection vials connected to
7 both outlets in order to both monitor and determine in real time the presence and the size
8 distribution of fullerene nanoparticles aggregates transported through the microchip.

9 Thanks to an optical fiber remote head, the system used in this work is a dedicated DLS
10 system for contact less in-situ measurement (see ESI, Fig S4). For the nanoparticles setup,
11 DLS specifications were: laser of 658 nm with a 60mW power; the scattering angle is 170°,
12 the working distance is fixed at 80 mm.

13 For nC₆₀ size kinetics determination with the NaCl, the intensity-weighted mean diameter (i.e.
14 called the z-average hydrodynamic diameter, d_{zH}) variation was used and was derived using
15 the *Cumulants* algorithm from the auto-correlation function (ACF)^{23,24}. *Cumulants* is the
16 simplest analysis of the ACF and is ideal to determine the average particle size of a
17 population. For obtaining size distribution from the autocorrelation curve (ACF function), two
18 algorithms were used: Sparse-Batesian-Learning (SBL) and the Cumulants. Cumulants
19 algorithm is one of the most famous and recognized method for determining size distribution
20 of polydisperse sample (Kopel). In the case of environmental and/or highly polydisperse
21 sample, Cumulants method presents several disadvantages. Indeed, this algorithm doesn't
22 permit independent determination of the long-time baseline of the ACF function and can lead
23 to inconsistent results when different numbers of data points are included in the fit. Using the
24 baseline as a floating parameter makes it possible to detect problems in the data and to fit data
25 when a little bit of noise is present, which our case. The d_H size distribution was determined
26 using the *Sparse Bayesian learning* (SBL) algorithm for the Laplace transform inversion²⁵.

1 This algorithm is adapted to identify, discriminate and determine the presence of several
2 polydisperse population from the ACF coming from the scattered light²⁵. More specifically, it
3 generates a set of sparse solutions of several domains but of the same dimension. Then, it
4 superimposes these solutions to give a global solution with its dimension treated as a
5 regularization parameter. An optimal solution providing a reliable description of a colloidal
6 suspension is determined by an L-curve for selecting the suitable value of the regularization
7 parameter. So, the final result corresponds to the most probable physical solution of the
8 algorithm which position is easily defined as the inflexion of a L-curve representation. This
9 method was proved to be more robust than classical methods used to determine size
10 distribution of polydisperse sample.

11

12 **Results and Discussion**

13 Here our objective is to show that the aggregate growth of nanoparticles depends strongly on
14 the homogeneity of the salt concentration. To do this we compare on Figure 2 the temporal
15 variation of the average hydrodynamic diameter, d_{zH} , of nC_{60} aggregates either obtained by
16 dropwise NaCl into the bulk, at two concentrations 85 and 500 mmol L⁻¹, (named bulk
17 experiments, BE), or collected at the outlets of our microfluidic device (named MD), A_{out} and
18 B_{out} , with an average salt concentration of 42 and 427 mmol L⁻¹, respectively. Both salt
19 concentration in the BE have been chosen to be very close to those obtained at the two outlets
20 of the MD. We choose the two salt concentrations in order to be on both sides of the critical
21 coagulation concentration (CCC) of nC_{60} , which is between 120 and 260 mM of sodium
22 chloride^{4-6,26} according to the different formation pathways²¹.

23 BE is generally performed to mimic the evolution of the aggregation features of nanoparticles
24 in salty natural environments, i.e., in the ocean or in Estuaries. In this case, the aggregation of
25 nC_{60} takes place in a spatially homogeneous salt concentration. Indeed the salt dispersed at

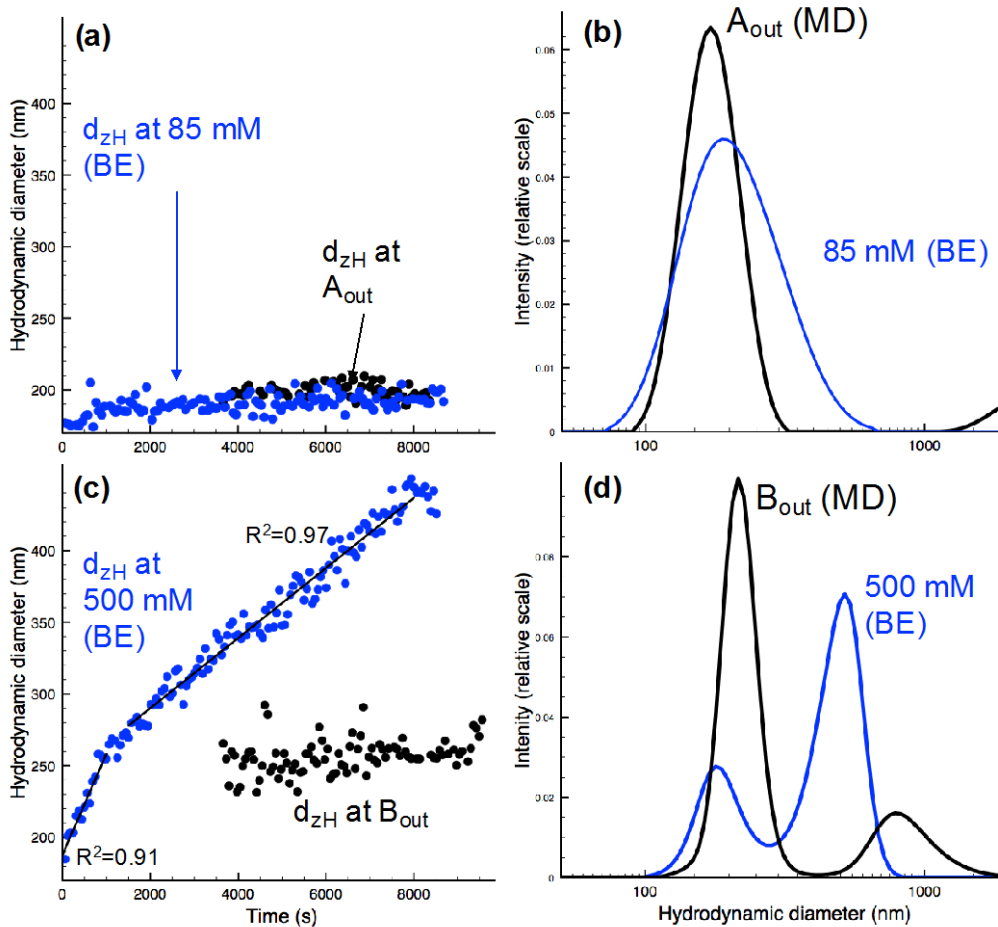
1 the beginning of the experiment diffuse so quickly throughout the vial that no significant
2 aggregates growth of nC_{60} is observed during this homogenization process. In the MD
3 experiment the fullerene aggregates (nC_{60}) quickly passed through a NaCl gradient and then
4 they can grow into a vial at rest, in the same conditions than those of the BE.

5 - Below the CCC of (nC_{60}) there is a slight increase of the aggregates sizes at the beginning of
6 the experiment ($t < 15$ min) for the BE and then there is no temporal evolution of d_{zH} anymore
7 (Fig. 2a, blue circle). The screening of the surface charge is limited at electrolyte
8 concentrations below the CCC and thus nC_{60} aggregation is limited. In this electrolyte
9 conditions, the nC_{60} suspension remains quite stable.

10 We found similar results for the microfluidic experiment in the outlet A_{out} (Fig. 2a, black
11 circle). This is further confirmed by looking at the global size distribution summed over the
12 total kinetics time for both types of experiment (Fig. 2b), which are very similar. The mean
13 aggregate size is a bit larger in the BE than in the MD experiment since the salt concentration
14 is slightly higher in the former case. However, it is worth noting that there is a small micron
15 size population ($d_{zH} > 1\mu m$) in the MD experiment, which is not the case in the BE. We will
16 get back to this point later on.

17 -Above CCC of (nC_{60}) the situation is completely different whether the nC_{60} aggregates
18 encounter a spatial salt gradient or not (Fig. 2c). In the BE d_{zH} increases over time, up to 400
19 nm. A similar trend was previously observed in literature, which validates our bulk
20 experiments strategy²⁶. As expected, above the CCC, the nanoparticle surface charge is
21 completely screened, thus eliminating the energy barrier to aggregation. Surprisingly, for
22 roughly the same amount of salt at the outlet B of the microchip there is only a limited
23 aggregate growth while we are well above the CCC, d_{zH} increasing slightly from 170 nm and
24 levels of around 260 nm. We do not observe any further growth after two hours. Two distinct
25 aggregate size distributions (Fig. 2d) were obtained for Bout and 500mM for the BE. For the

1 BE, the first population at 170 nm corresponds to the initial population of nC₆₀, while the
2 second population at 450 nm corresponds to the nC₆₀ aggregates induced by NaCl. This
3 means that one part of the nC₆₀ aggregates that belongs to this initial population has not yet
4 partake to the aggregation process. If the experiment would have last longer this first
5 population would have disappeared progressively. In the MD experiment we also have two
6 aggregate populations. However in the MD experiment, contrary to BE, the initial population
7 is predominant in the size distribution. There is only a slight shift of the average aggregate
8 size, from 170 to 250 nm. Therefore in this case the aggregation mechanism is quite different
9 than before, for the BE. Moreover, as for A_{out}, a micro-sized population is still observed but
10 with much larger contribution to the overall population of B_{out}. We suppose that there is a
11 release of micron-sized aggregates of nC₆₀ formed in the MD. Nevertheless, their quantity is
12 relatively low compare to the nano-sized population (170 nm) due to the dependence of
13 intensity of light scattered (I) with size (r^6) and concentration c .



1

2 *Figure 2: (a,c) illustration of the z-average hydrodynamic diameter (nm), determined by the Cumulants algorithm,*
 3 *according to the ionic strength using bulk experiment and the use of MD (A_{out} and B_{out}) (b,d) the average hydrodynamic*
 4 *diameter distribution determined by SBL algorithm and integrated along the whole duration of the kinetics (8500 and 4500 s*
 5 *for bulk an MD experiments, respectively). On (c) for 500 mM (BE), there are two linear fits of the data ($d_{zH} = a.T$, with*
 6 *$a=0.064$ and $a=0.023$ for larger values).*

7

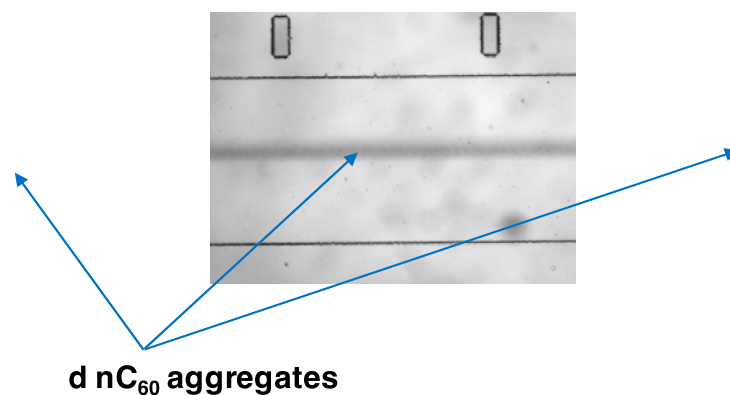
8 Several hypotheses can be made to explain the difference between the particle aggregation in
 9 the bulk and the microfluidic experiment.

- 10 ○ First, the difference between microfluidics and the bulk experiments could be
- 11 explained by the Diffusion-Limited Colloidal Aggregation (DLCA) and Reaction-
- 12 Limited Colloidal Aggregation (RLCA) mechanisms²⁷. Indeed, it is well known that in
- 13 batch mode, DLCA is the predominant behavior, where no repulsive barrier exists
- 14 between the particles and the aggregate growth rate is entirely driven by Brownian
- 15 motion. DLCA induces the formation of open structure aggregates, with fractal
- 16 dimension (D_f) generally ranging between 1.5 and 2.0 with a linear increase of the

1 aggregate size over time ^{5,26}, as we also obtained here (Fig. 2.c). In the other case,
2 where there is a repulsive energy barrier between fullerene particles, RLCA is
3 dominant with a limited aggregate growth, contrary to DLCA, as it was observed in
4 case of the microfluidic experiment presented in this work. This result suggests that
5 the salt gradient causes the nC_{60} aggregation according to the RLCA mode and
6 thereafter remains stable in time over our experimental window.

- 7 ○ Secondly, during the transportation of nC_{60} through the microchip, after several hours
8 of experiments and replicates larger aggregates can be formed in the salt front
9 localized at the center of the channel corresponding to the black line in fig. 3.

10 Indeed, this black-like deposition is characteristic of fullerene aggregates and is
11 localized at the middle of the salt gradient. If too large aggregates could be formed,
12 the micron-sized fraction of those sediment into the MD (Fig. 3). This hypothesis
13 would confirm that micron-sized particles released in A_{out} and B_{out} are aggregates
14 formed mainly within the salinity gradient in the MD. Nevertheless, this hypothesis
15 cannot explain why the other part of the size distribution, small particles still present
16 in B_{out} at high $[NaCl]$ (i.e. $>CCC$), do not form greater aggregates over time, as big as
17 those observed in bulk experiments.



18 **d nC_{60} aggregates**
19 *Figure 3: Illustration of the MD with deposition of nC_{60} micron-sized aggregates in the center of the channel (dark lines)*
20 *after several cycles of operation and replicates*

1

2 Due to the NaCl concentrations used in this study, no representative electronic microscopy
3 image of the nC₆₀ aggregates can be obtained. But, despite the different hypotheses described
4 above, it appears clearly that nC₆₀ are transported and diffused through the salinity gradient.
5 During this short time transportation within the salinity gradient, a clear difference on the
6 aggregation behavior is identified, compared to the classical results in bulk experiments.

7

8 **Environmental implication**

9

10 Based on these results and comparing to the literature concerning the environmental behavior
11 of manufactured nanomaterials, several questions raised up. Indeed, both incidental and
12 manufactured nanoparticles are expected to be released massively closed to urban system that
13 will be eventually released in the river and finally transport through the estuarine system
14 characterized by an increasing ionic strength. The expectations are that nanoparticles (NPs)
15 will settle at different rate when the ionic strength increases. In literature, physical phenomena
16 occurring in estuarine area, such as the salinity gradient and various flow conditions, were
17 never considered. But, our results suggest that a short exposition of NP such as nC₆₀ within
18 the salinity gradient affects definitely their aggregation mechanisms, and therefore their
19 environmental behavior. Secondly, the scientific community on colloids and nanoparticles
20 agrees to the fact that an ionic strength closed to the seawater ones leads to an irreversible
21 aggregation and a change in size (up to micrometer). Our results suggest that the salinity
22 gradient could enhanced the stability of nanoparticles, especially at high ionic strength (closed
23 to the seawater one). This first study shows the need to reconsider the spatial and temporal
24 variation of abiotic parameters (ionic strength, pH, organic matter concentration) in the

1 understanding and the evaluation of nanoparticles environmental fate and transportation
2 mechanisms.

3

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6 National Center for Scientific Research (CNRS; LaCUNE and LaCUNE-2 projects) and the
7 Brittany Council of France (SAD program, NANOSALT project).

8

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