## Field deployable reactors for investigating the interaction of nanoparticles with natural organic matter under field conditions

\* Corresponding author

Authors: Narjes Tayyebi Sabet Khomami <sup>a</sup>, Allan Philippe <sup>a\*</sup>, Abd Alaziz Abu Quba <sup>a</sup>, Oliver J. Lechtenfeld <sup>b,c</sup>, Jean-Michel Guigner <sup>d</sup>, Stefan Heissler <sup>e</sup>, Gabriele E. Schaumann <sup>a</sup>

<sup>a</sup> iES Landau, Institute for Environmental Sciences, Fortstrasse 7, 76829 Landau, Germany. <sup>b</sup> UFZ - Helmholtz-Centre for Environmental Research, Department Analytical Chemistry, Research Group BioGeoOmics, 04318 Leipzig, Germany. <sup>c</sup> ProVIS – Centre for Chemical Microscopy, UFZ – Helmholtz-Centre for Environmental Research, 04318 Leipzig, Germany. <sup>d</sup> IMPMC, Sorbonne University, CNRS – UMR 7590, MNHN, Paris, France. <sup>e</sup> Institute of Functional Interfaces IFG, Karlsruhe Institute of Technology KIT, Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany.

**Table S1:** Properties of the river water used for the laboratory and field experiments (May-September 2018).

| Date               | Conductivity<br>(µs/cm) | рН  | DOC (mg/l)        | Stream flow<br>rate (cm/s) <sup>1</sup> | Temp.<br>C | Dissolved<br>oxygen<br>(mg/l) |
|--------------------|-------------------------|-----|-------------------|---|------------|-------------------------------|
| Late May           | 271                     | 7.2 | $6.1(\pm 0.16)^2$ | -                                       | -          | -                             |
| Mid Jun            | 301                     | 7.1 | $8.2(\pm 0.42)^2$ | -                                       | -          | -                             |
| Mid July           | 280                     | 7.1 | $6.1(\pm 0.37)^2$ | -                                       | -          | -                             |
| Late July          | 293                     | 7.4 | $6.7(\pm 0.21)^2$ | -                                       | -          | -                             |
| Late September     | 272                     | 7.2 | $6.5(\pm 0.15)^2$ | $32.3(\pm 7.5)^2$                       | 21         | $8.79(\pm 1.23)^2$            |
| (field experiment) |                         |     |                   |   |            |                               |

<sup>1</sup>One meter from the river bank

<sup>2</sup>Standard deviation

| Elements | Concentration | LOD (µg/l) | Standard      |
|----------|---------------|------------|---------------|
|          | (µg/l)        |            | deviation (%) |
| Al       | 16.5          | 1          | 1.20          |
| Ba       | 43.5          | 0.5        | 3.02          |
| Ca       | 5246.0        | 1          | 0.35          |
| Cu       | < LOD         | 0.5        | -             |
| Fe       | 20.3          | 1          | 2.80          |
| Ti       | < LOD         | 0.05       | -             |
| Κ        | 509.4         | 2.5        | 0.80          |
| Mg       | 1030.2        | 0.5        | 0.15          |
| Mn       | 2.7           | 0.3        | 0.01          |
| Na       | 3227.1        | 25         | 0.33          |
| Sr       | 93.4          | 0.5        | 0.13          |
| Zn       | 1.6           | 0.5        | 6.25          |

**Table S2:** Total concentration of selected elements in the river water determined using ICP-OES (September 2018). LOD: limit of detection.

**Table S3:** Anions concentrations of the river water using ion chromatography (September 2018). LOD: limit of detection.

| Anions    | Concentration | LOD (mg/l) | Standard      |
|-----------|---------------|------------|---------------|
|           | (mg/l)        |            | deviation (%) |
| Fluoride  | 0.04          | 0.02       | 4.0           |
| Chloride  | 10.11         | 0.65       | 4.5           |
| Nitrate   | 4.94          | 0.67       | 3.0           |
| Phosphate | 0.148         | 0.08       | 3.5           |
| Sulphate  | 20.98         | 1.61       | 5.4           |



Figure S1: The cellulose ester dialysis bag (cylindrical design) used in this study.



Figure S2: The dialysis bags in plastic canisters deployed in the river Queich.



**Figure S3:** Assessment of the instrumental variability based on replicate measurements of SRFA (n = 6). Normalized intensity values were used to calculate the relative standard deviation (RSD). 95 % of the RSD values were below 0.303.



Figure S4: AFM height image of the dialysis bag in river water, and river water exposed to n-TiO<sub>2</sub>.



Figure S5: AFM phase image of the dialysis bag in river water, and river water exposed to n-TiO<sub>2</sub>.



**Figure S6**: Fluorescence EEMs of the samples carried out in the field C) river water inside the dialysis bags with  $n-TiO_2$  (the color scale depicts the intensity a.u).



**Figure S7:** Euler diagram depicting the distribution of molecular formulas detected by FT-ICR-MS in all three samples (outside the dialysis bag, and inside the dialysis bag with and without  $n-TiO_2$ ) deployed on the field.

| Sample                      | СНО  | CHNO | CHOS | CHNOS | Other |
|-----------------------------|------|------|------|-------|-------|
| River water (inside)        | 2677 | 1777 | 472  | 91    | 5     |
| 0⁄0                         | 53.3 | 35.4 | 9.4  | 1.8   | 0.1   |
| River water (outside)       | 2443 | 1565 | 537  | 116   | 7     |
| 0⁄0                         | 52.3 | 33.5 | 11.5 | 2.5   | 0.1   |
| n-TiO <sub>2</sub> (inside) | 2906 | 1927 | 534  | 138   | 4     |
| %                           | 52.8 | 35.0 | 9.7  | 2.5   | 0.1   |

**Table S4:** Major compound class distribution of all three samples deployed on the field based on the molecular formulas determined using FT-ICR-MS.



**Figure S8:** Van Krevelen diagram with intensity differences for river water inside the dialysis bags with n-TiO<sub>2</sub> vs without n-TiO<sub>2</sub>.  $\Delta$ RI values below 0.43 (blue) indicate the respective compound is depleted in the river water inside the dialysis bag with n-TiO<sub>2</sub> compared to without n-TiO<sub>2</sub>.



**Figure S9:** DOC and Dissolved oxygen of the river water inside dialysis bags (DB) with and without n-TiO<sub>2</sub>, and the river water as control with and without n-TiO<sub>2</sub> at room temperature (Nov. 2019).



Figure S10: ATR-FTIR spectrum of the river water (freeze-dried sample).