

Supporting Information

Depth-dependent Transformation of ZnO and Ag Nanoparticles in Sulfate-reducing Sediments Tracked using Scanning Transmission Electron Microscopy

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This file contains 21 pages, 19 figures and 2 tables.

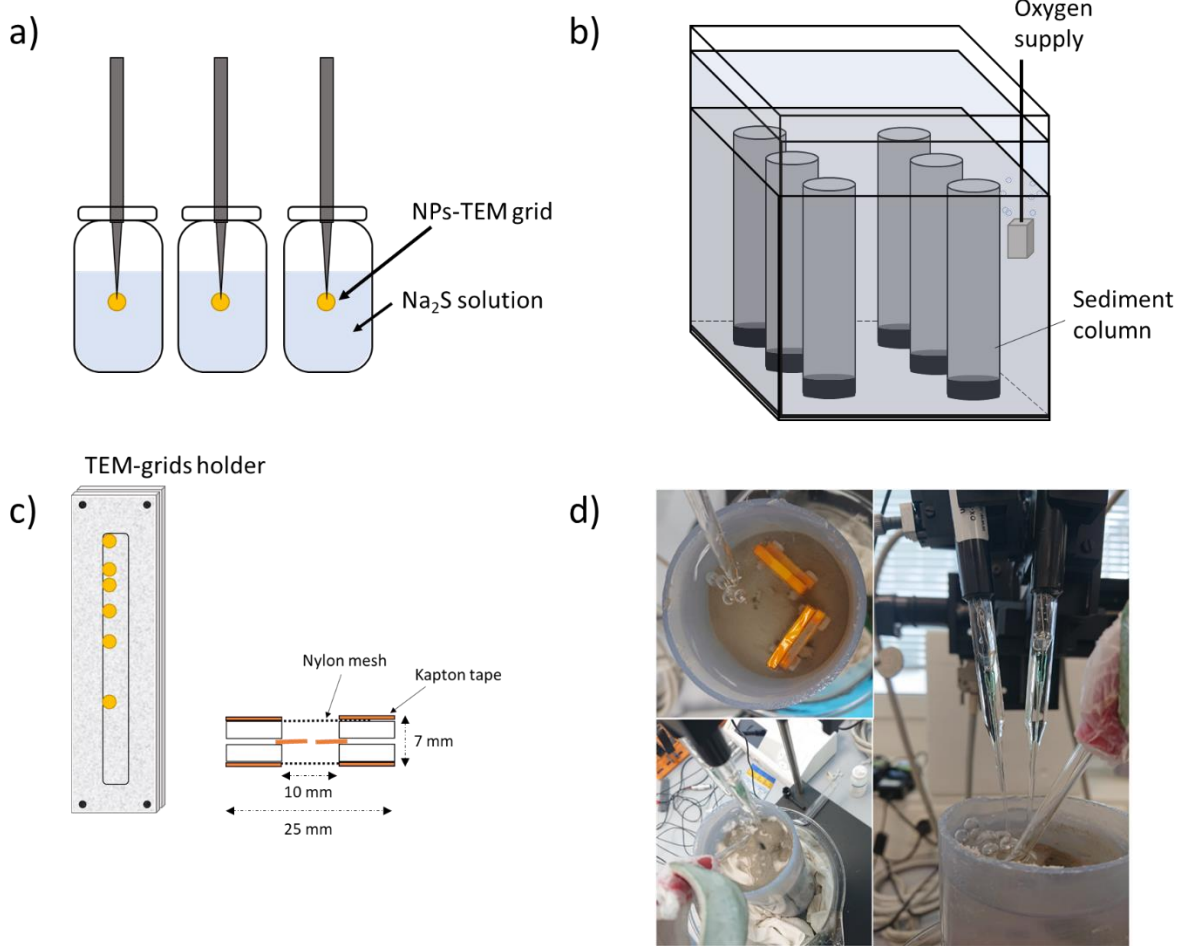


Figure SI-1: Illustrations of the experimental setups used for (a) the exposure experiments in sodium sulfide (Na₂S) solutions and (b) the exposure experiments in incubated sediment columns. (c) Illustrations of the TEM grid sample holder inserted in the sediment columns. (d) Photos of the experimental design showing TEM grid sample holders within a sediment column and the O₂ and pH microelectrodes.

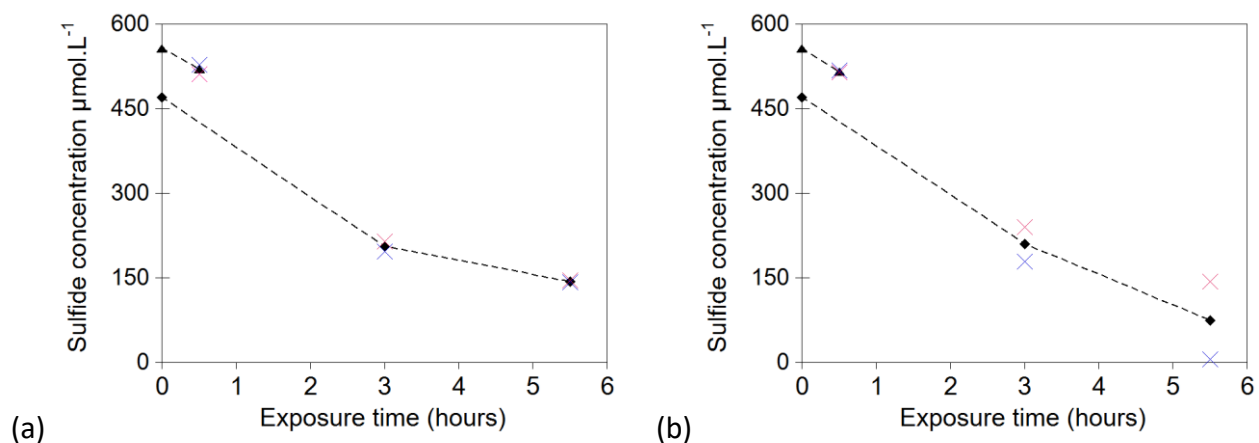


Figure SI-2: Averaged sulfide concentrations measured in the (a) Ag NPs and (b) ZnO NPs batches over the course of the experiments in Na_2S solutions. The blue and red crosses correspond to the concentrations measured in duplicates A and B, respectively.

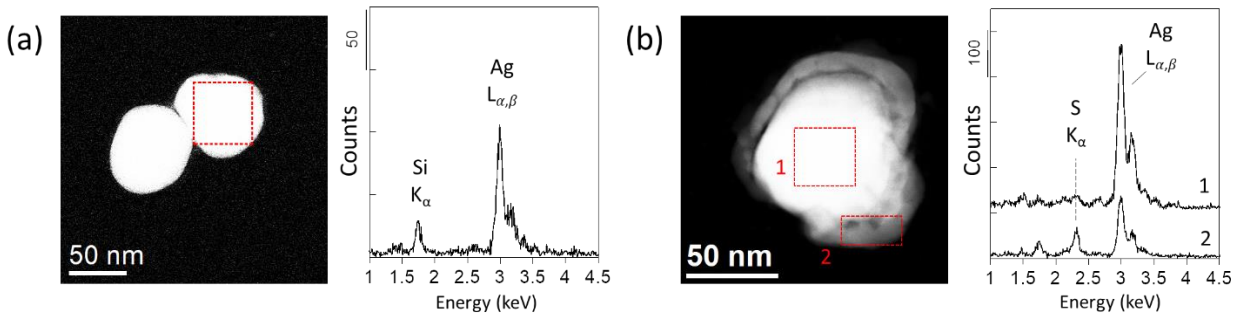


Figure SI-3: (a) STEM micrograph acquired in high-angle annular dark-field detector (HAADF) mode of pristine Ag NPs after one day of storage, and corresponding EDX spectrum (b) STEM micrograph acquired in HAADF mode of a pristine Ag NPs after 4.5 days of storage in a TEM grid vacuum desiccator and corresponding EDX spectrum.

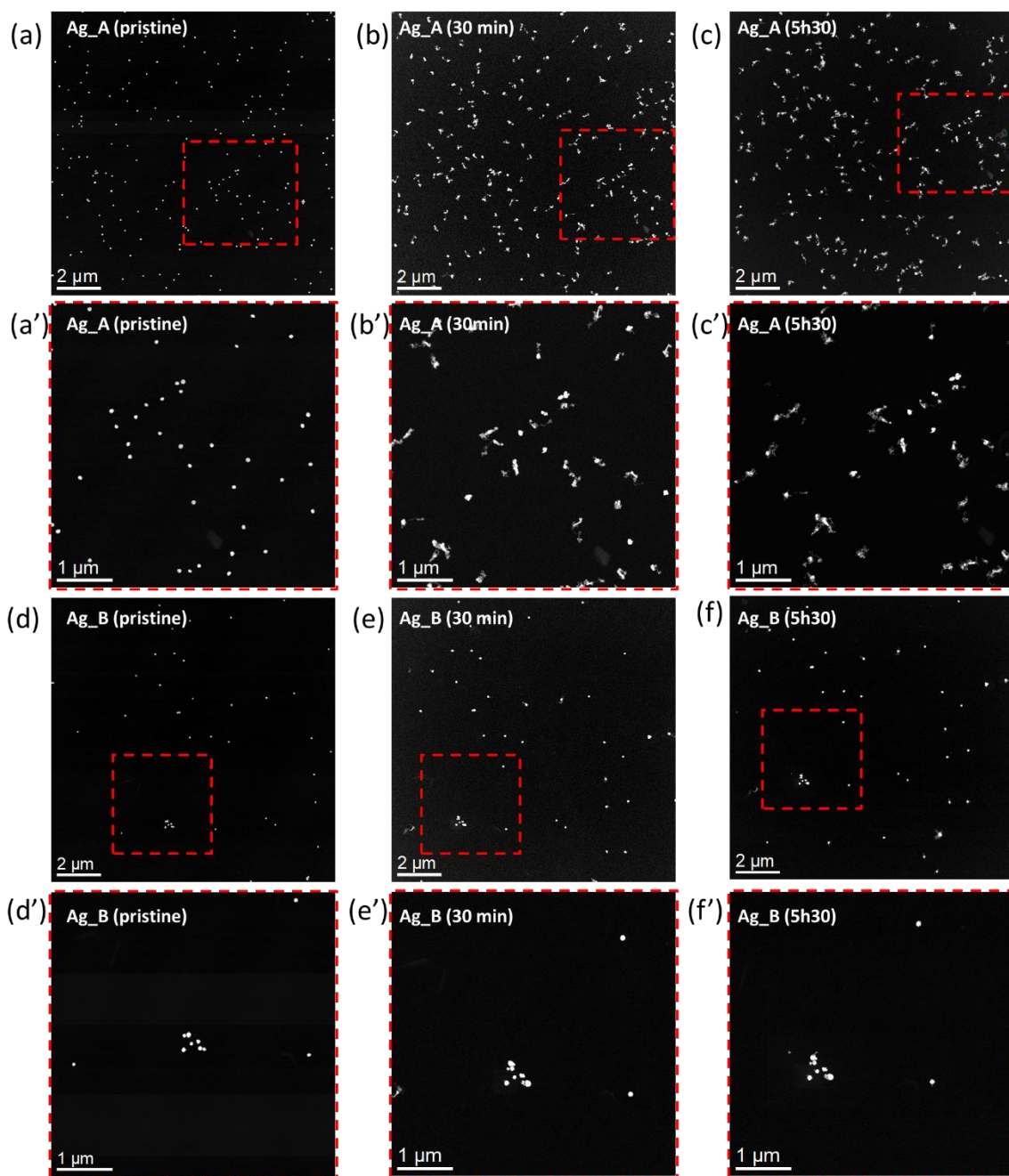


Figure SI-4: STEM micrographs of Ag NPs before (a,a'd,d'), after 30 min (b,b',e,e'), and after 5h30 (c,c',f,f') of exposure in the 500 μM Na_2S solution at pH 7.5 for the duplicates A and B. Images were recorded with a HAADF detector. After 30 minutes, three ROIs per duplicate were investigated. After 5 hours and 30 minutes, one of the ROI was re-investigated for each duplicate.

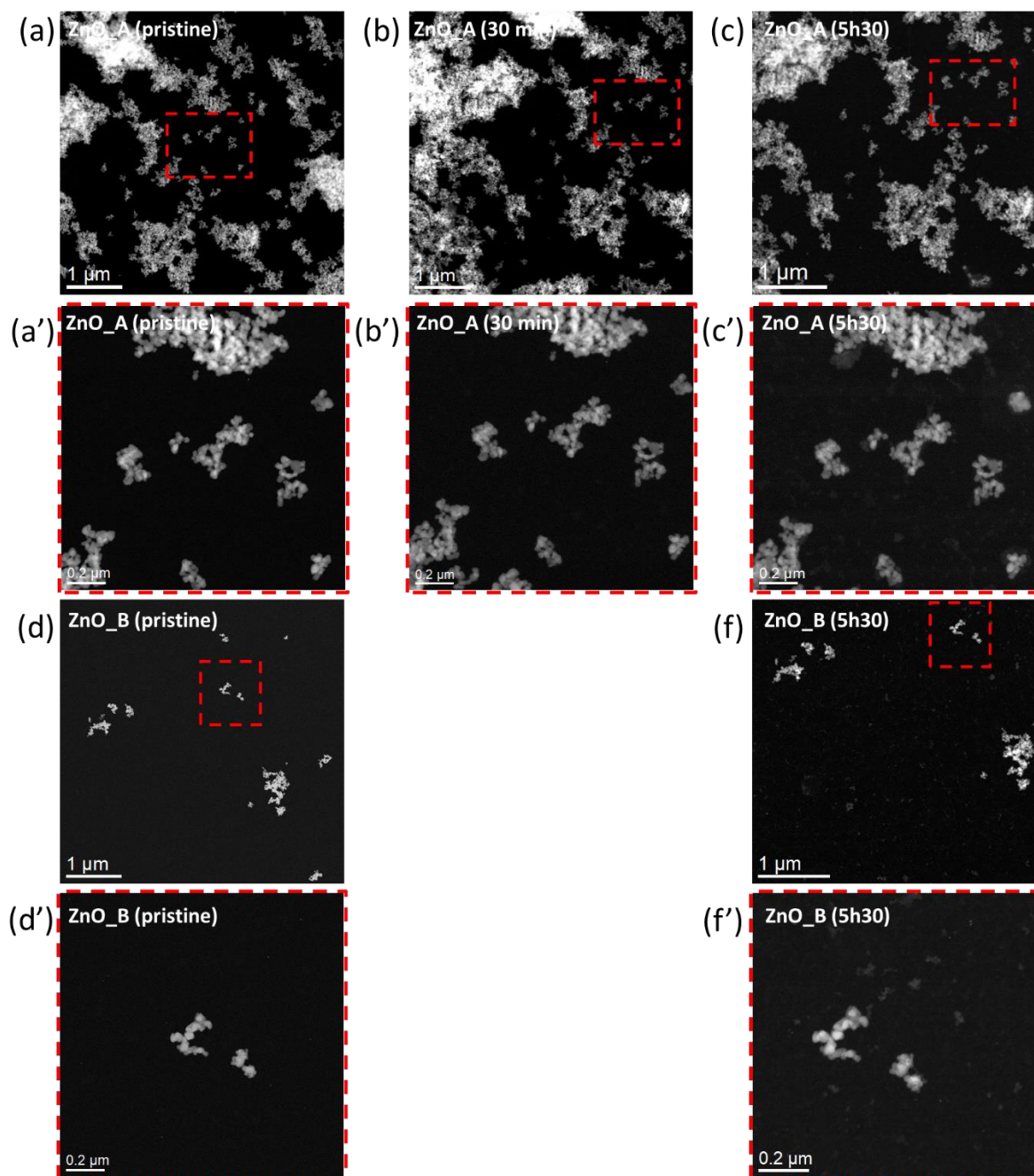


Figure SI-5: STEM micrographs of ZnO NPs before (a,a'd,d'), after 30 min (b,b'), and after 5h30 (c,c',f,f') of exposure in the 500 μM Na_2S solution at pH 7.5 for the duplicates A and B. Images were recorded with a HAADF detector. After 30 minutes, one ROI was investigated on sample ZnO_A. After 5 hours and 30 minutes, the same ROI was re-investigated in sample ZnO_A and two ROIs were investigated in sample ZnO_B.

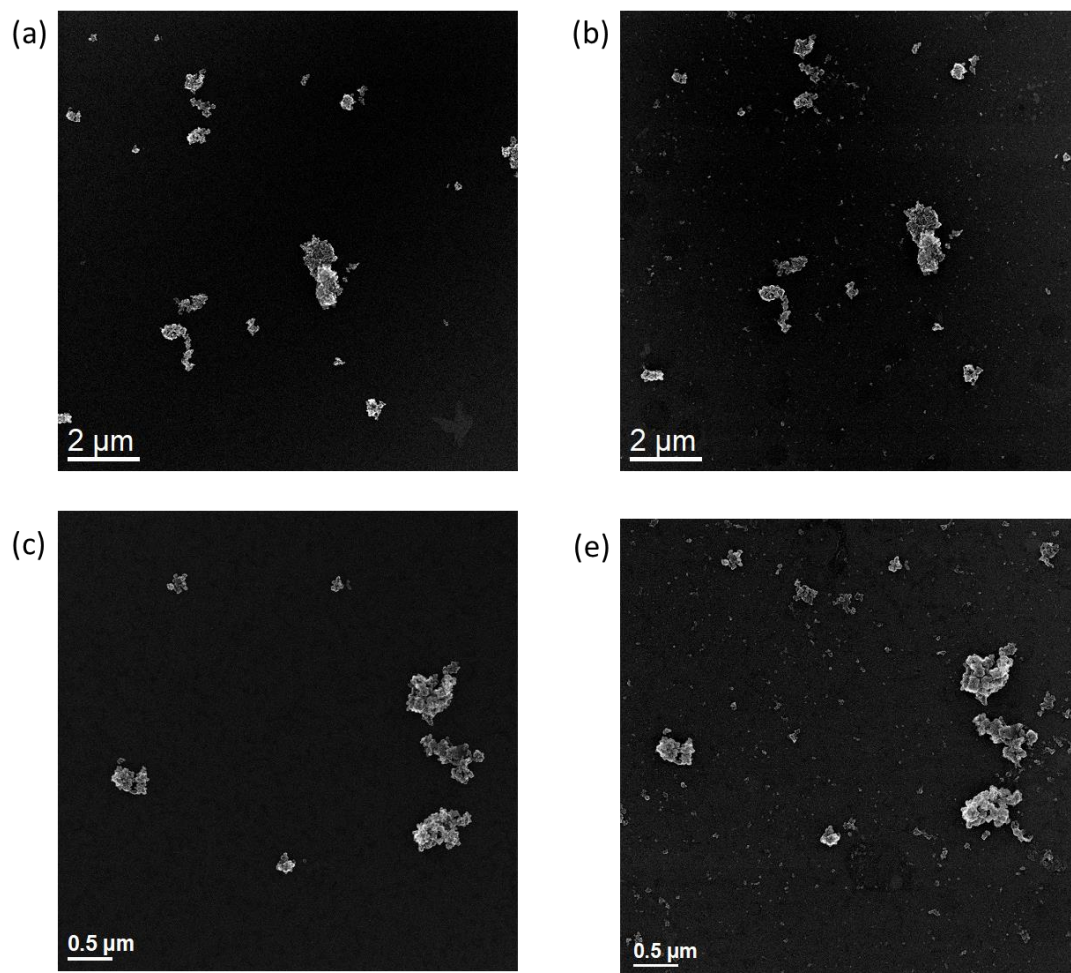


Figure SI-6: STEM micrographs of ZnO NPs (a,c) before and (b,d) after 5h30 of exposure in the 500 μM Na₂S solution at pH 7.5. Images were recorded with a secondary electron (SE) detector on the sample ZnO_B.

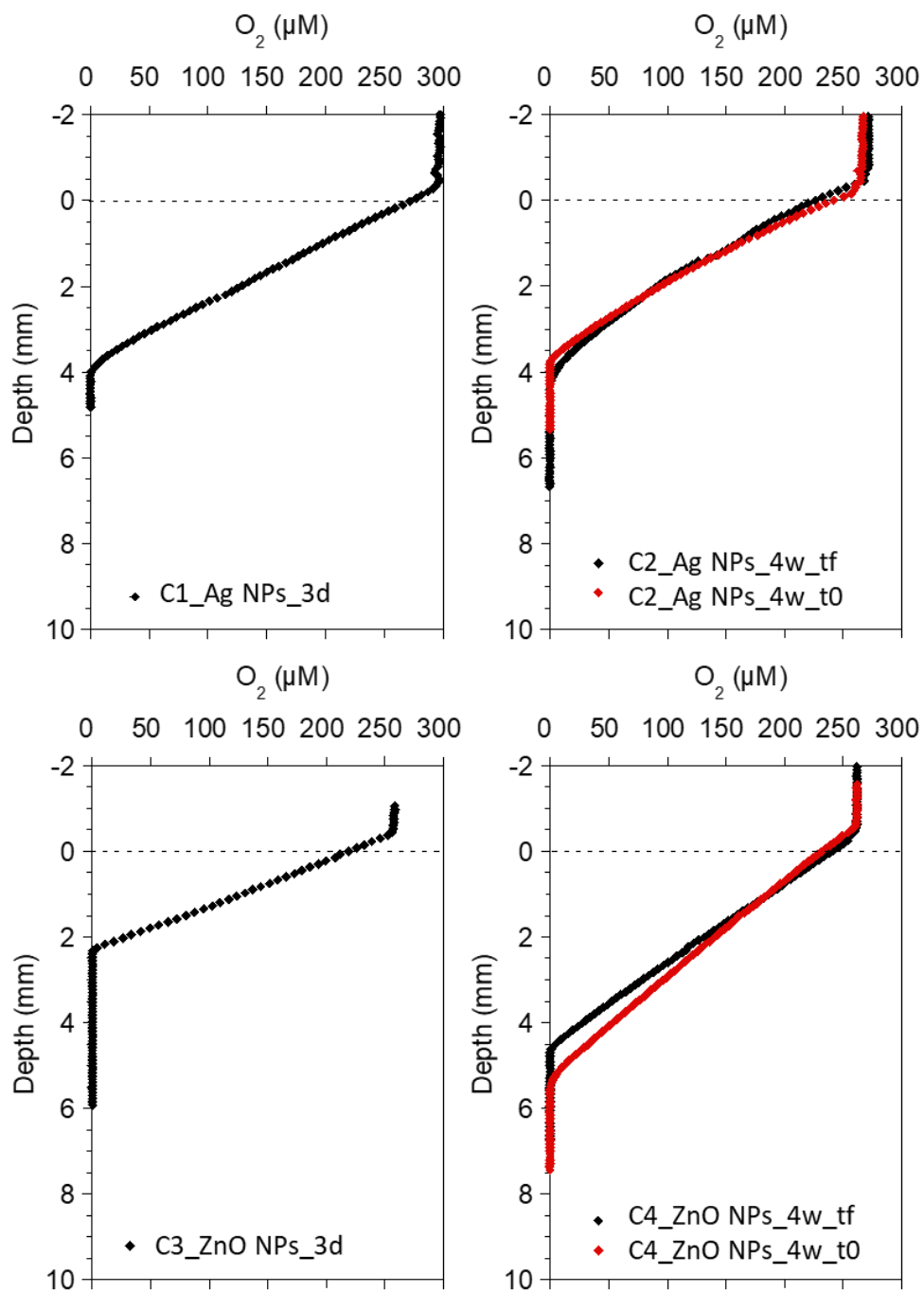


Figure SI-7: Oxygen concentration depth profiles at the water-sediment interfaces of the sediment cores used for the exposure experiments.

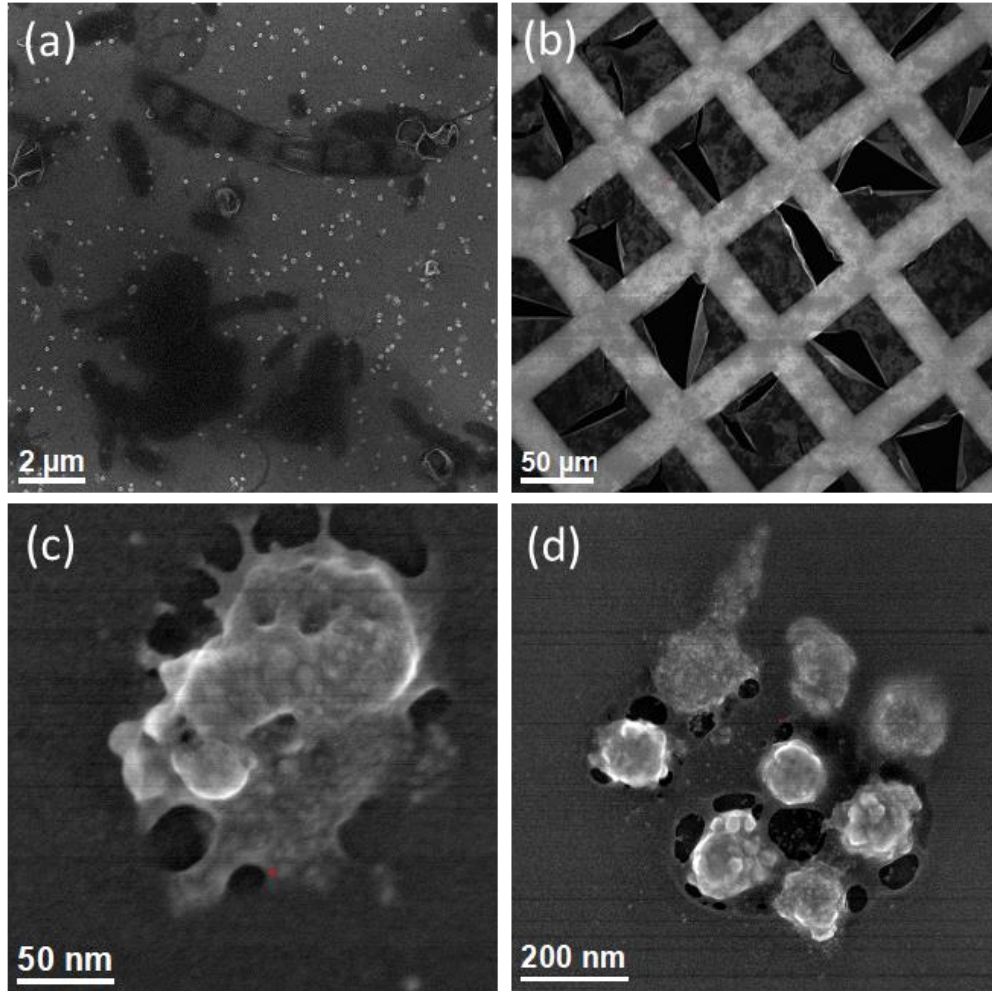


Figure SI-8: Ag NPs exposed (a) at 7-10mm and (b,c,d) at 0-3mm during four weeks, showing damages and contamination on the TEM grids after the exposure in the sediment. Micrographs were acquired with a SE detector. (a) sample Ag_7-10mm_4w_a (b,c,d) sample Ag_0-3mm_4w_b.

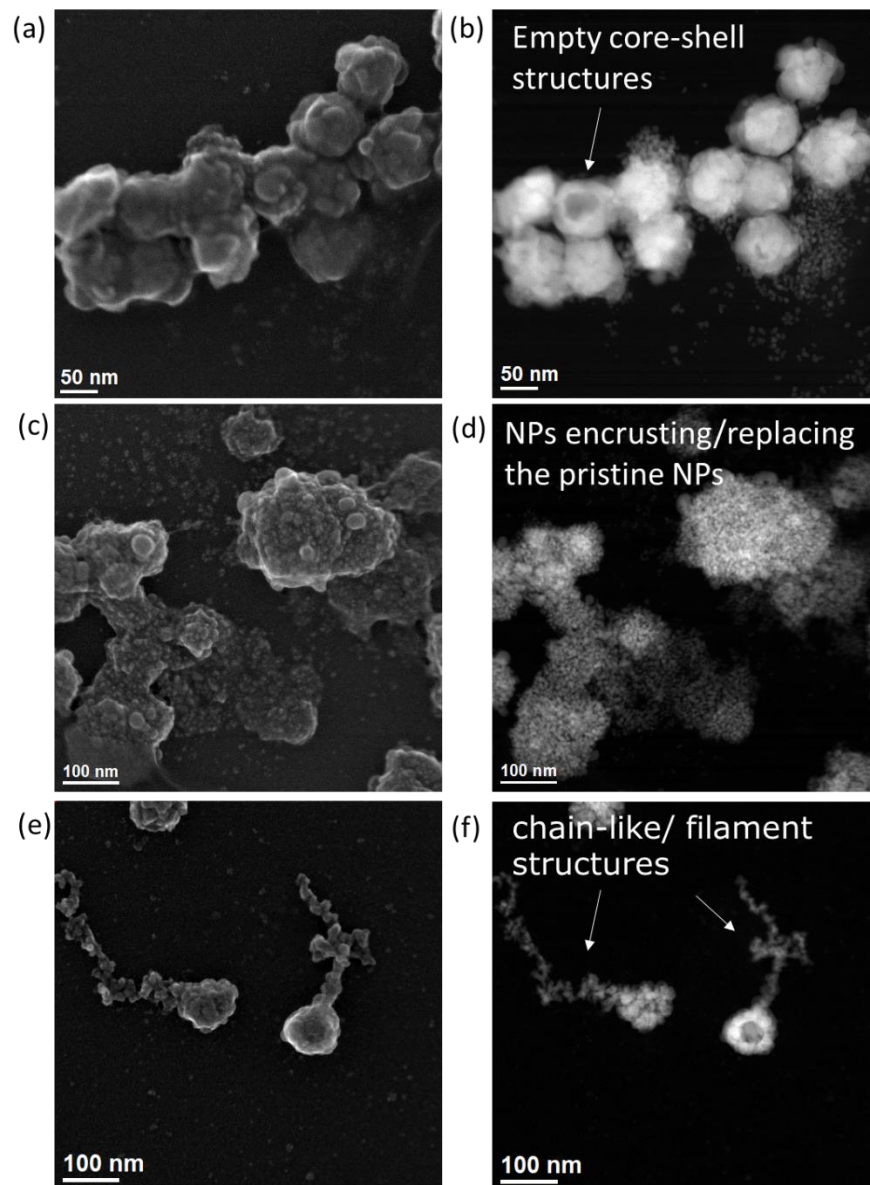


Figure SI-9: STEM micrographs of Ag NPs exposed at (a,b,c,d) 0-3 mm and (e,f) 60 mm depth during four weeks, representing the various morphologies observed for Ag-sulfides. Micrographs were acquired with (a,c,e) a SE detector, and with (b,d,f) a HAADF detector. (a,b,c,d) sample Ag_0-3mm_4w_a (e,f) sample Ag_60mm_4w_b.

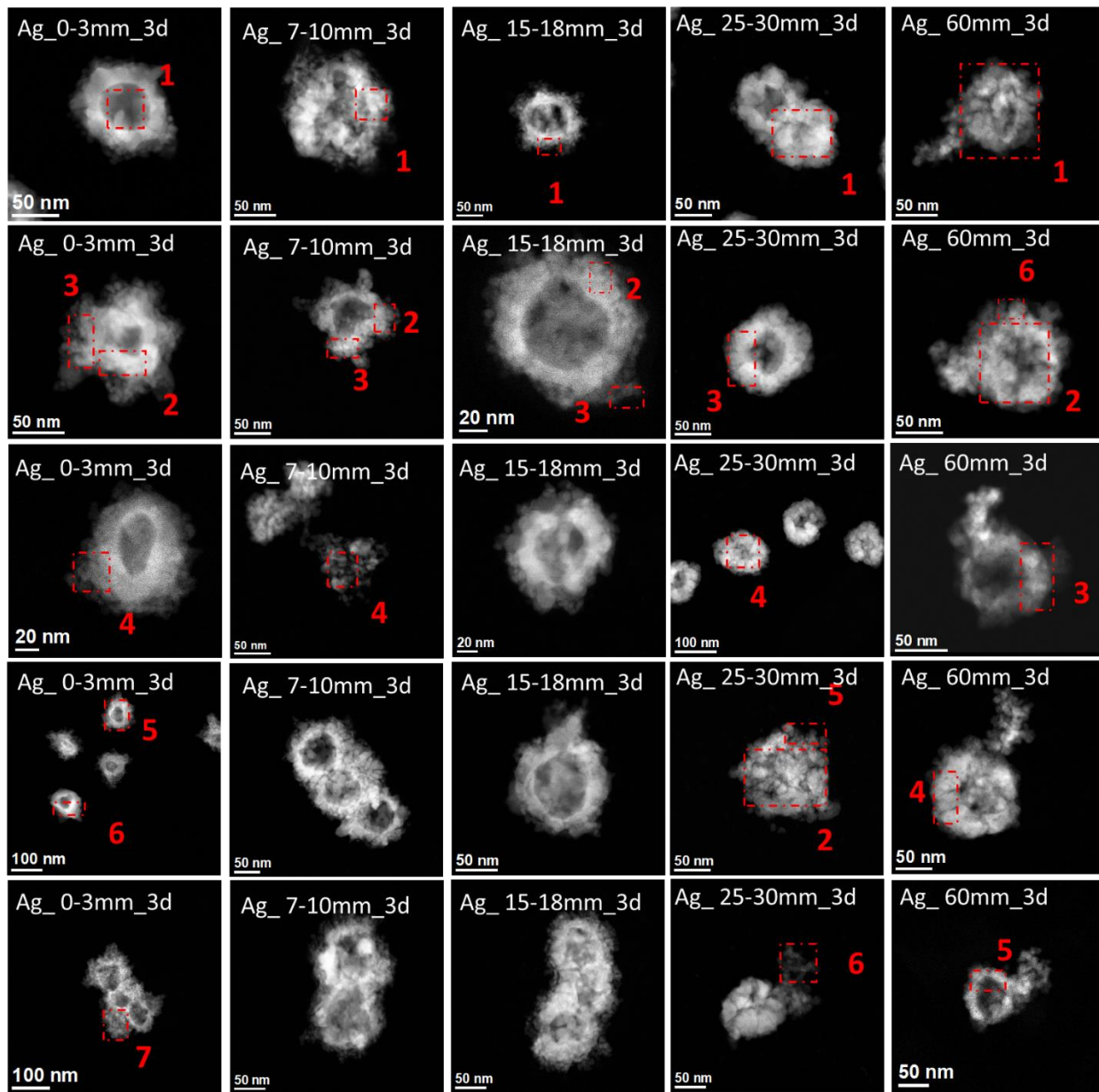


Figure SI-10: STEM micrographs of Ag NPs exposed for three days in the sediment column C1. Micrographs were acquired with a HAADF detector. The name of the sample is displayed on each micrograph. The dotted red squares correspond to the scanned area for the EDX analyses. The corresponding EDX spectra are presented in Figure SI-11.

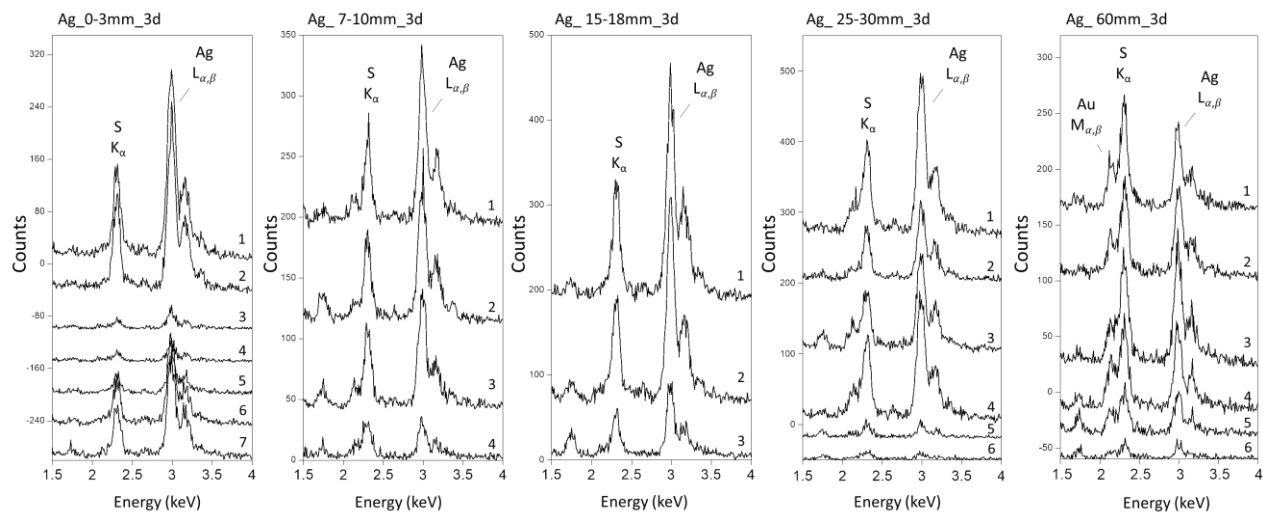


Figure SI-11: EDX spectra of Ag NPs exposed for three days in the sediment column C1. Each EDX spectrum corresponds to a scan area presented in Figure SI-10.

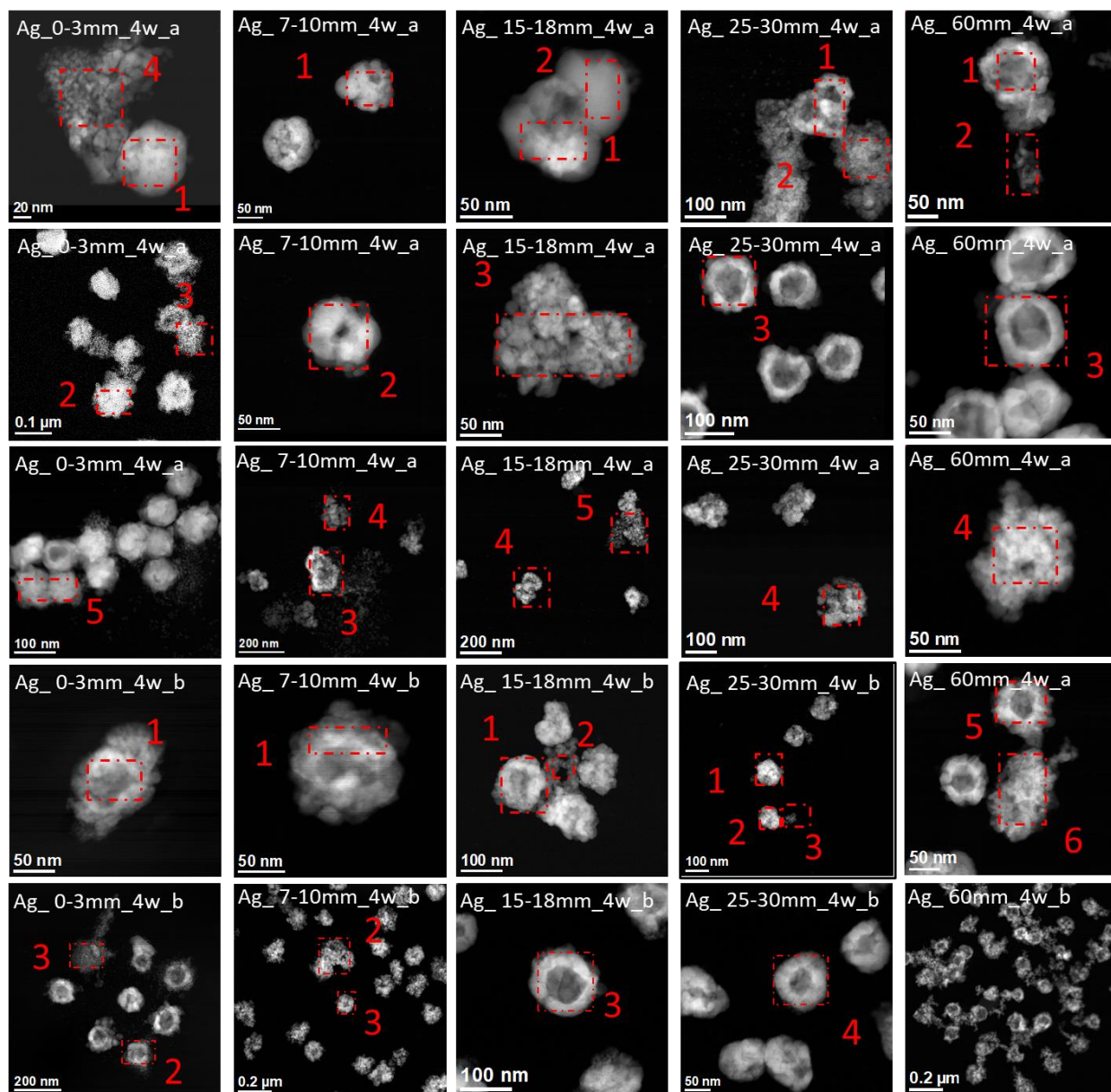


Figure SI-12: STEM micrographs of Ag NPs exposed for four weeks in the sediment column C2. Micrographs were acquired with a HAADF detector. The name of the samples is displayed on each micrograph. The dotted red squares correspond to the scanned area for the EDX analyses. The corresponding EDX spectra are presented in Figure SI-13.

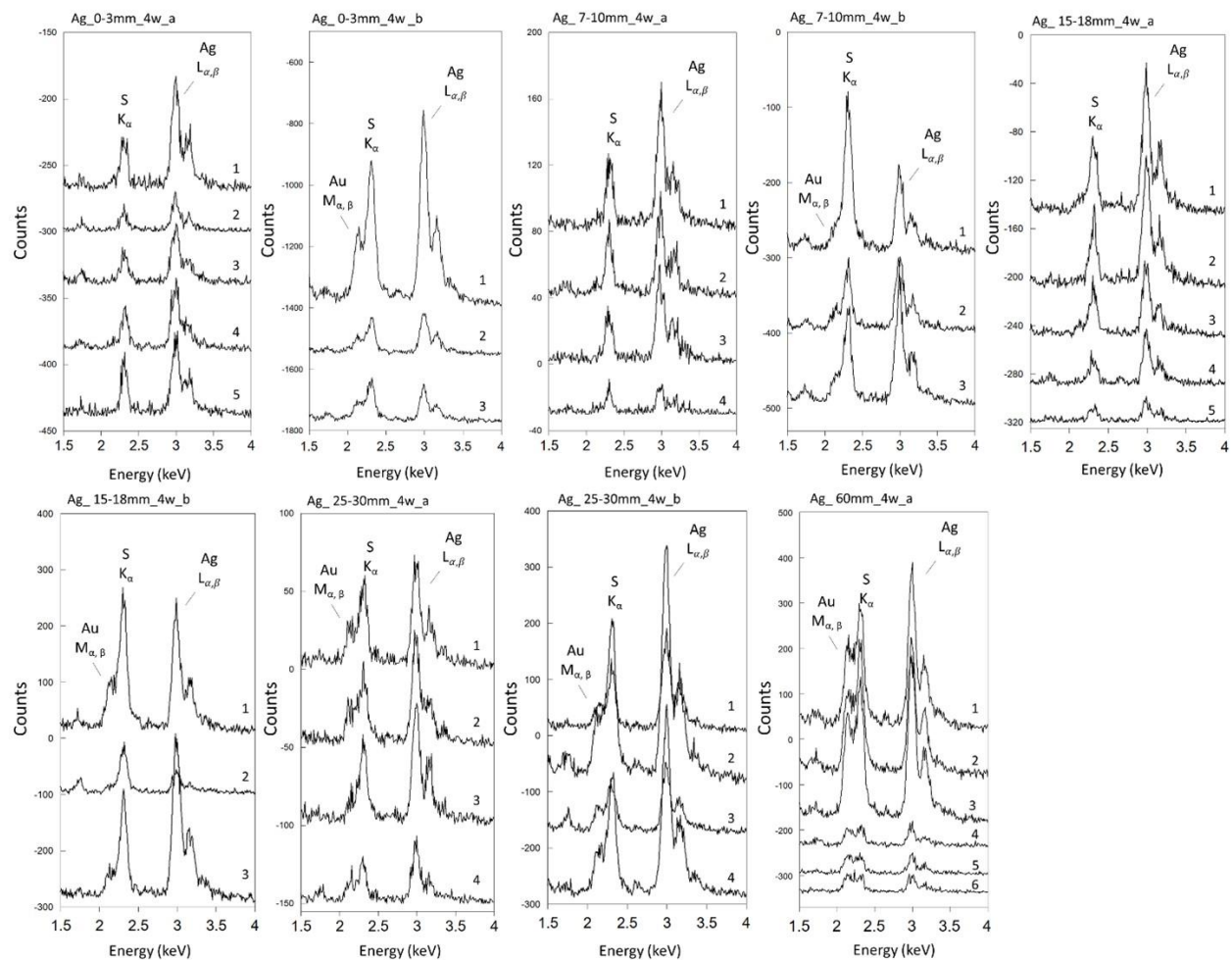


Figure SI-13: EDX spectra of Ag NPs exposed for four weeks in the sediment column C2. Each EDX spectrum corresponds to a scan area presented in Figure SI-11.

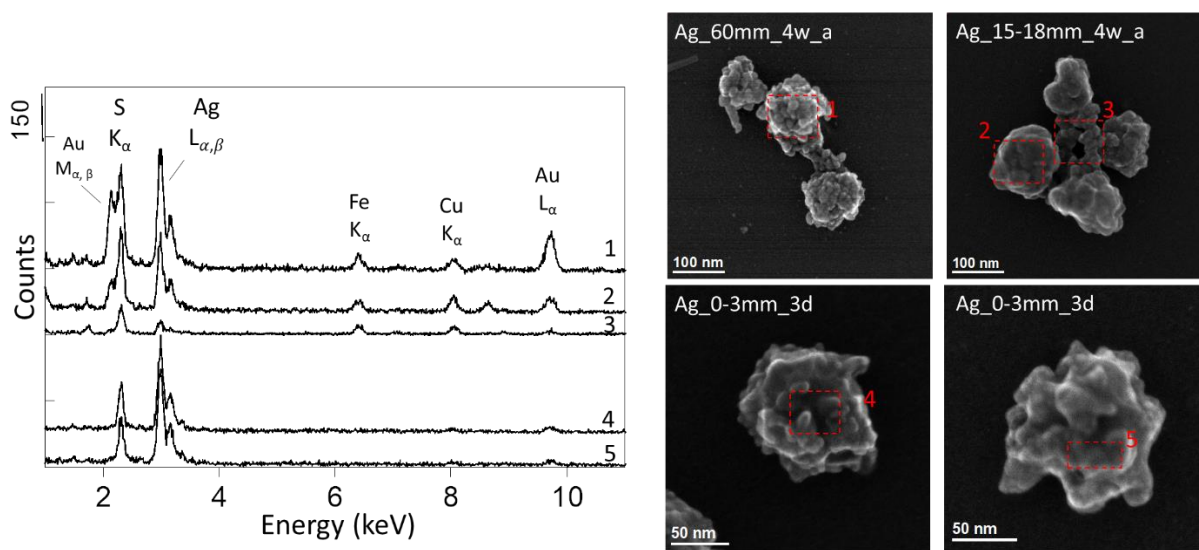


Figure SI-14: (a) STEM micrographs acquired on the samples Ag_60mm_4w_a, Ag_15-18mm_4w_a, and Ag_0-3mm_3d with a SE detector, and corresponding EDX spectra.

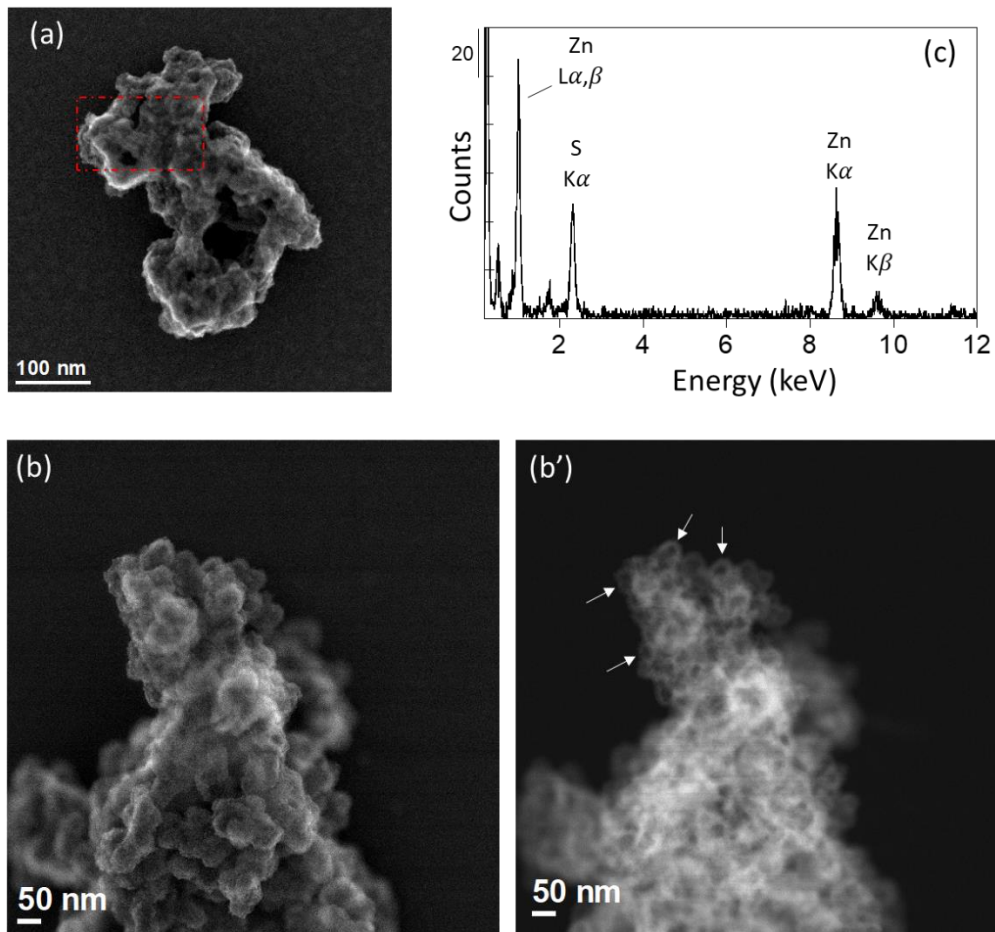


Figure SI-15: (a,b,b') STEM micrographs acquired in (a,b) SE mode and (b') in HAADF mode of ZnO NPs exposed at 0-3 mm depth during three days. The dotted red square corresponds to the scanned area for the EDX analysis. The white arrows help for the visualization of small empty ZnS shell structures.

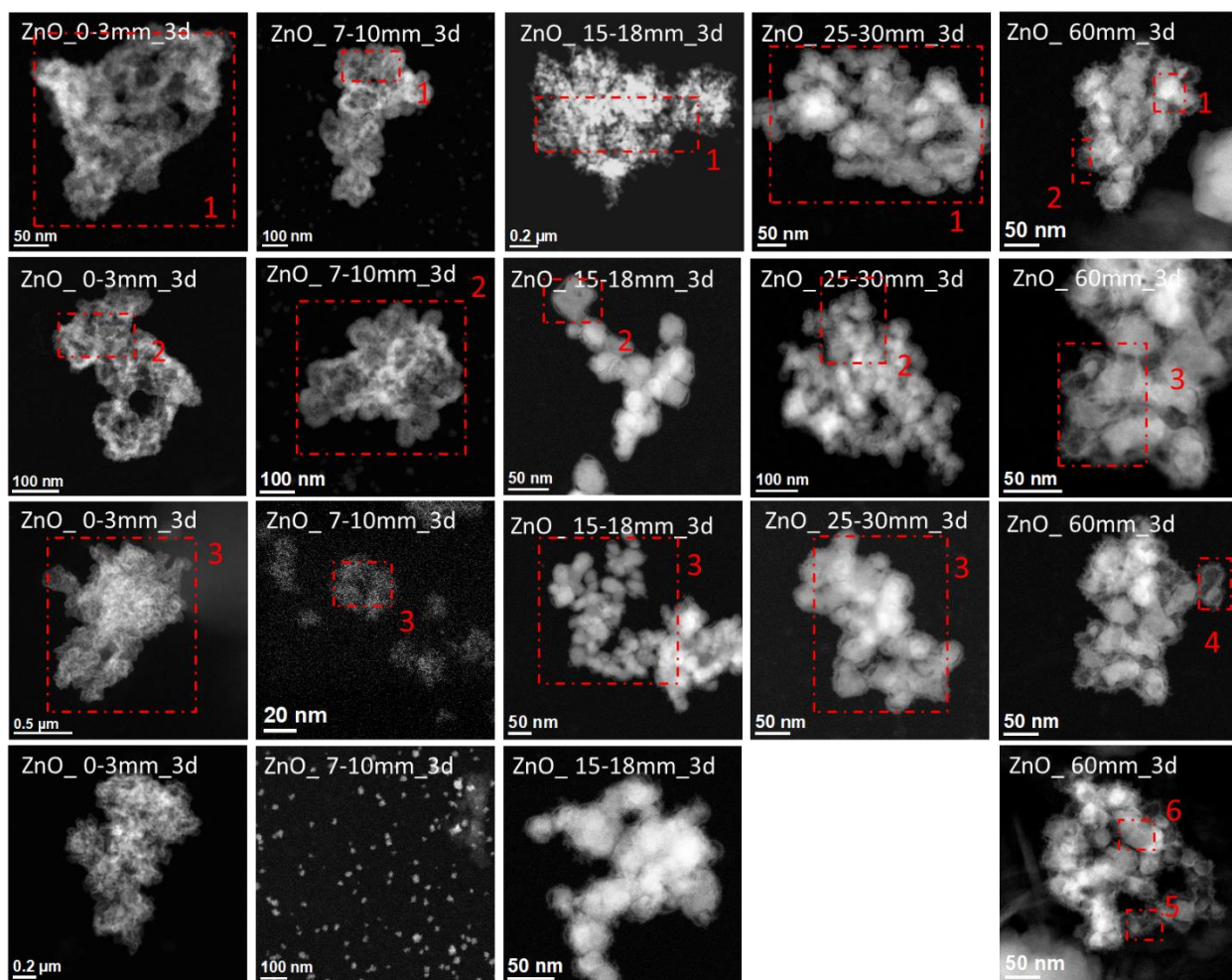


Figure SI-16: STEM micrographs of ZnO NPs exposed for three days in the sediment column C3. Micrographs were acquired with a HAADF detector. The name of the sample is displayed on each micrograph. The dotted red squares correspond to the scanned area for the EDX analyses. The corresponding EDX spectra are presented in Figure SI-17.

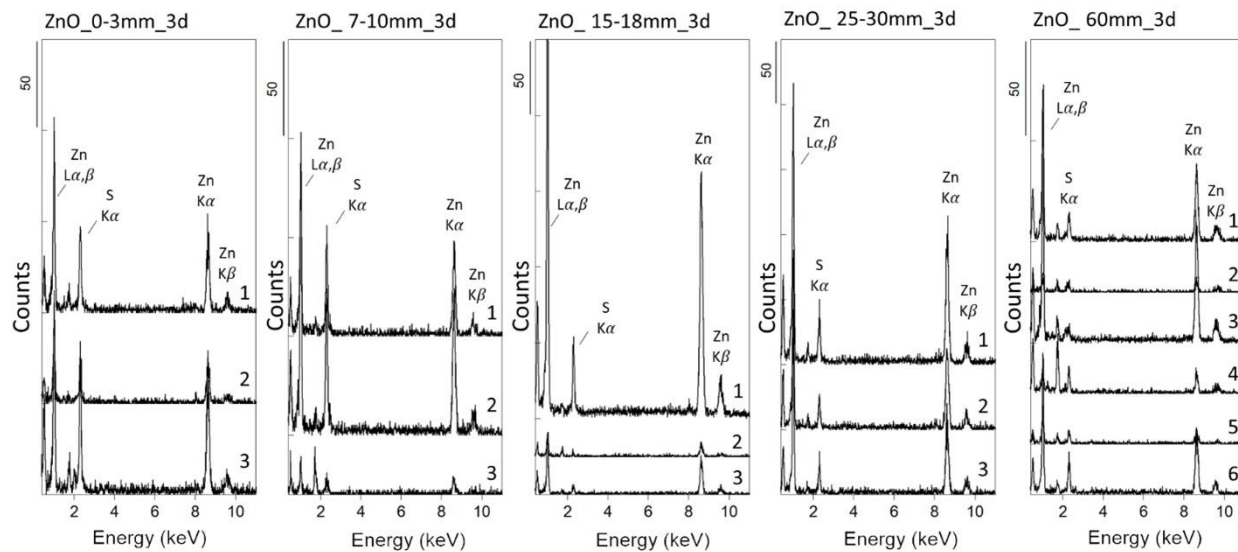


Figure SI-17: EDX spectra of ZnO NPs exposed for three days in the sediment column C3. Each EDX spectrum corresponds to a scan area presented in Figure SI-16.

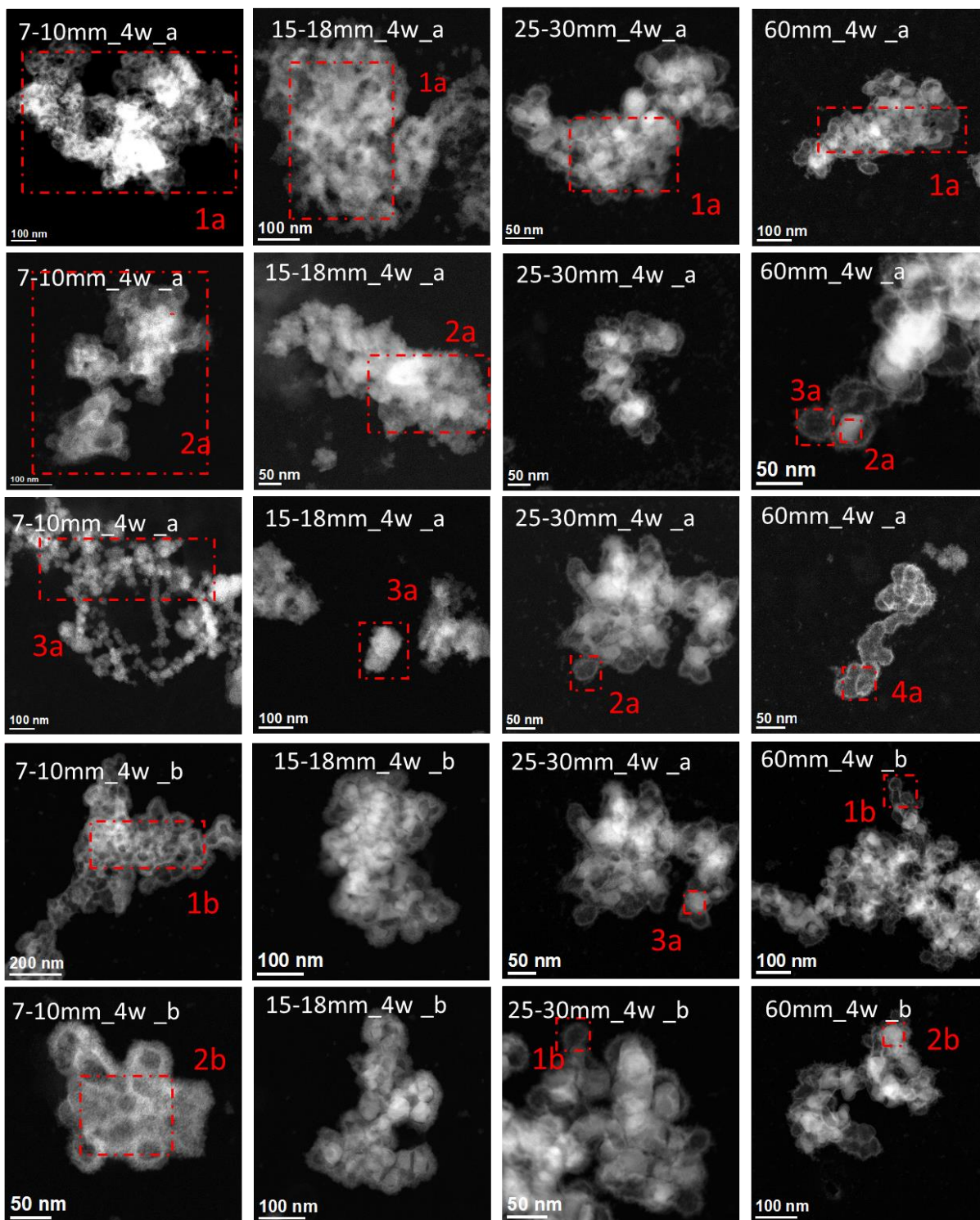


Figure SI-18: STEM micrographs of ZnO NPs exposed for four weeks in the sediment column C4. Micrographs were acquired with a HAADF detector. The name of the samples is displayed on each micrograph. The dotted red squares correspond to the scanned area for the EDX analyses. The corresponding EDX spectra are presented in Figure SI-19.

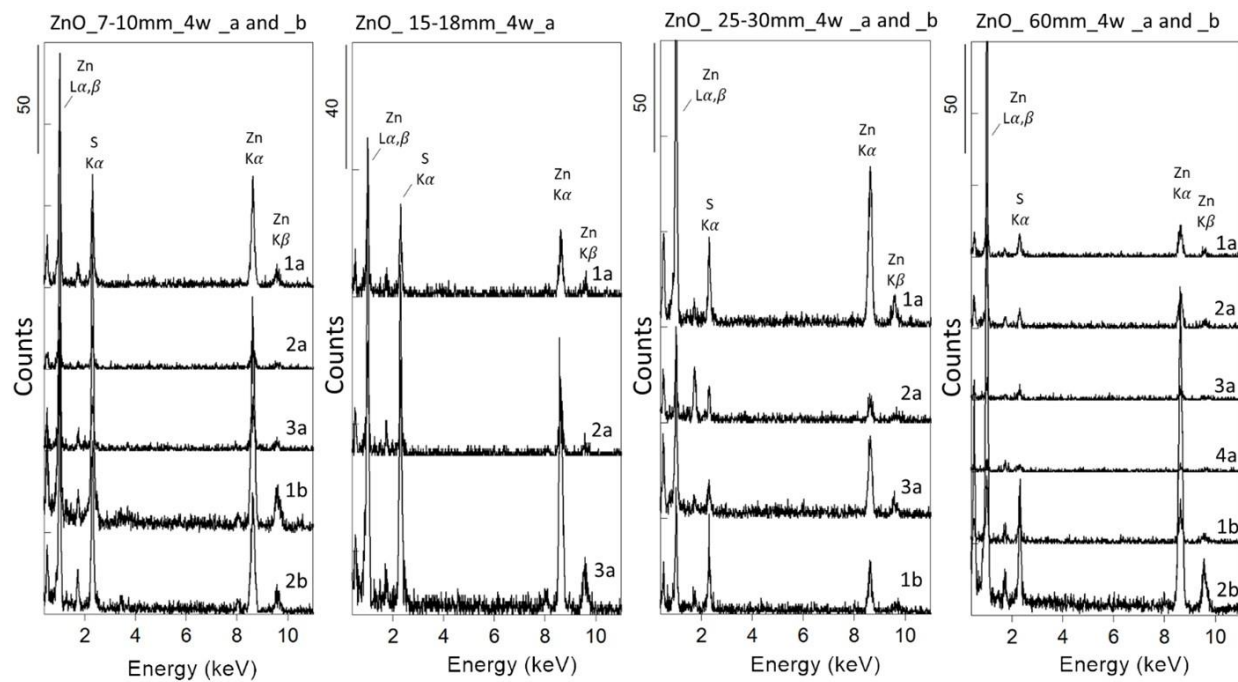


Figure SI-19: EDX spectra of ZnO NPs exposed for four weeks in the sediment column C4. Each EDX spectrum corresponds to a scan area presented in Figure SI-18.

Table SI-1: Number of Ag NPs analyzed by STEM-EDX after the three days and four weeks experiments in the sediment columns.

Sample name	Depth (mm)	Total of NPs examined
<i>Core C1 - Ag NPs exposure during 3 days</i>		
Ag_0-3mm_3d	0-3	Imaging : 23 NPs Imaging + EDX analysis: 7 NPs
Ag_7-18mm_3d	7-10	Imaging : 16 NPs Imaging + EDX analysis: 4 NPs
Ag_15-18mm_3d	15-18	Imaging : 12 NPs Imaging + EDX analysis: 3 NPs
Ag_25-30mm_3d	25-30	Imaging : 8 NPs Imaging + EDX analysis: 7 NPs
Ag_60mm_3d	60	Imaging : 7 NPs Imaging + EDX analysis: 7 NPs
<i>Core C2 - Ag NPs exposure during 4 weeks</i>		
Ag_0-3mm_4w_a	0-3	Imaging : 40 NPs Imaging + EDX analysis: 10 NPs
Ag_0-3mm_4w_b	0-3	Imaging : 58 NPs Imaging + EDX analysis: 10 NPs
Ag_7-10mm_4w_a	7-10	Imaging : 30 NPs Imaging + EDX analysis: 5 NPs
Ag_7-10mm_4w_b	7-10	Imaging : 55 NPs Imaging + EDX analysis: 7 NPs
Ag_15-18mm_4w_a	15-18	Imaging : 12 NPs Imaging + EDX analysis: 6 NPs
Ag_15-18mm_4w_b	15-18	Imaging : 51 NPs Imaging + EDX analysis: 6 NPs
Ag_25-30mm_4w_a	25-30	Imaging : 54 NPs Imaging + EDX analysis: 4 NPs
Ag_25-30mm_4w_b	25-30	Imaging : 23 NPs Imaging + EDX analysis: 7 NPs
Ag_60mm_4w_a	60	Imaging : 66 NPs Imaging + EDX analysis: 11 NPs
Ag_60mm_4w_b	60	Imaging : 37 NPs Imaging + EDX analysis: -

Table SI-2: Number of ZnO NPs analyzed by STEM-EDX after the three days and four weeks experiments in the sediment columns.

Sample name	Depth (mm)	Total of NPs examined
<i>Core C3 - ZnO NPs exposure during 3 days</i>		
ZnO_0-3mm_3d	0-3	Imaging : 3 NPs Imaging + EDX analysis: 3 NPs
ZnO_7-18mm_3d	7-10	Imaging : 4 NPs Imaging + EDX analysis: 3 NPs
ZnO_15-18mm_3d	15-18	Imaging : 3 NPs Imaging + EDX analysis: 4 NPs
ZnO_25-30mm_3d	25-30	Imaging :- NPs Imaging + EDX analysis: 3 NPs
ZnO_60mm_3d	60	Imaging : 2 NPs Imaging + EDX analysis: 4 NPs
<i>Core C4 - ZnO NPs exposure during 4 weeks</i>		
ZnO_0-3mm_4w_a	0-3	No NPs remaining on the grids
ZnO_0-3mm_4w_b	0-3	No NPs remaining on the grids
ZnO_7-10mm_4w_a	7-10	Imaging : - NPs Imaging + EDX analysis: 5 NPs
ZnO_7-10mm_4w_b	7-10	Imaging : 2 NPs Imaging + EDX analysis: 2 NPs
ZnO_15-18mm_4w_a	15-18	Imaging : 4 NPs Imaging + EDX analysis: 3 NPs
ZnO_15-18mm_4w_b	15-18	Imaging : 3 NPs Imaging + EDX analysis: 1 NPs
ZnO_25-30mm_4w_a	25-30	Imaging : 1 NPs Imaging + EDX analysis: 3 NPs
ZnO_25-30mm_4w_b	25-30	Imaging : 2 NPs Imaging + EDX analysis: 1 NPs
ZnO_60mm_4w_a	60	Imaging :3 NPs Imaging + EDX analysis: 3 NPs
ZnO_60mm_4w_b	60	Imaging : - NPs Imaging + EDX analysis: 4 NPs