Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Supplementary information

Size Dependence of Silver Nanoparticle Removal in a Wastewater Treatment Plant Mesocosm Measured by FAST Single Particle ICP-MS

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Monitored chemical parameters

The data in figures SI-1 – SI-3 shows the monitored chemical parameters ordered according to the date of experiment. The 15/10/2013, 05/11/2013, and 06/11/2013 are the experiments 1,2, and 3 discussed in the main text. Data from the rest of the experiments, when no useful spICP-MS data could be obtained, are shown for the sake of completeness.

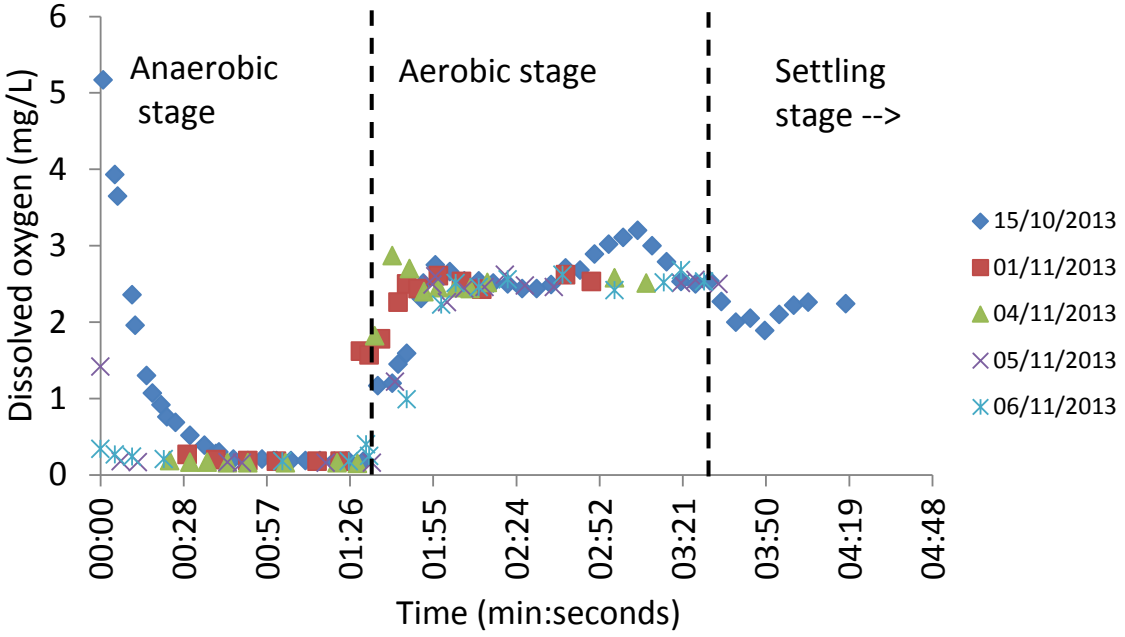

Figure SI-1. Dissolved oxygen as a function of time during the WWTP mesocosm runs. The oxygen during the settling stage was measured only for the first experiment because of fear of stirring the sample.

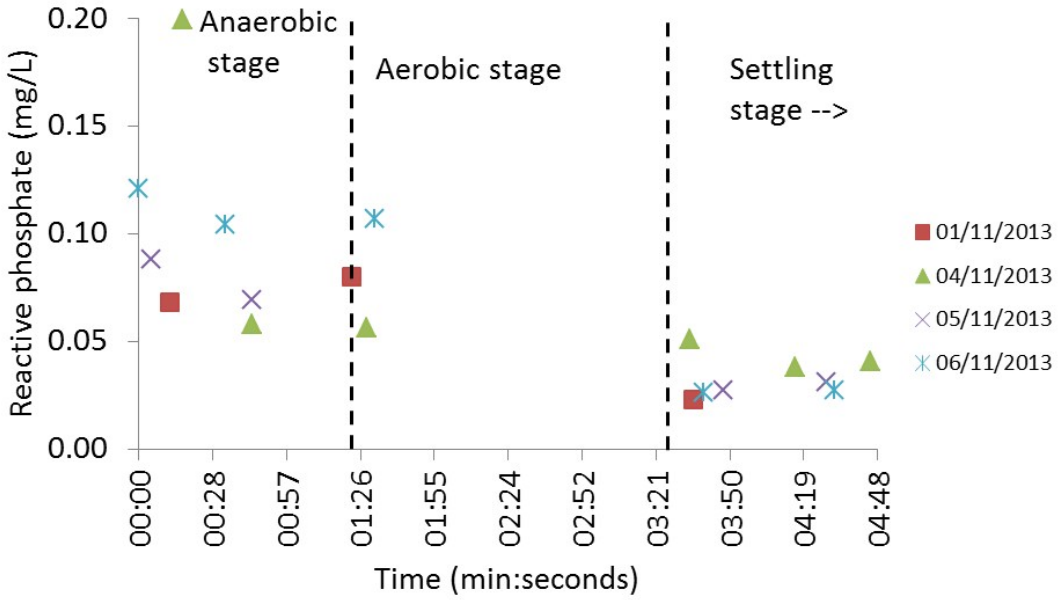

Figure SI-2. Reactive phosphate concentration as a function of time during the WWTP microcosm runs. Note that no such measurements were done on the 15/10/2013 run when analyses failed.

Figure SI-3 shows other parameters (pH, conductivity, anions). Except for nitrate and nitrite, these parameters were not varying with time, and average values are therefore shown for each run and the standard deviations are shown as error bars. The pH was near neutral for all runs and conductivity did not vary either. Nitrate and nitrite was present at high concentration at the time of spiking, but were quickly depleted during the anaerobic stage. During this stage oxygen is depleted first and then microorganisms switch to nitrate to serve as electron acceptor, upon which all nitrate is quickly depleted, followed by an equally rapid depletion of nitrite. The concentrations did not vary after this initial phase.

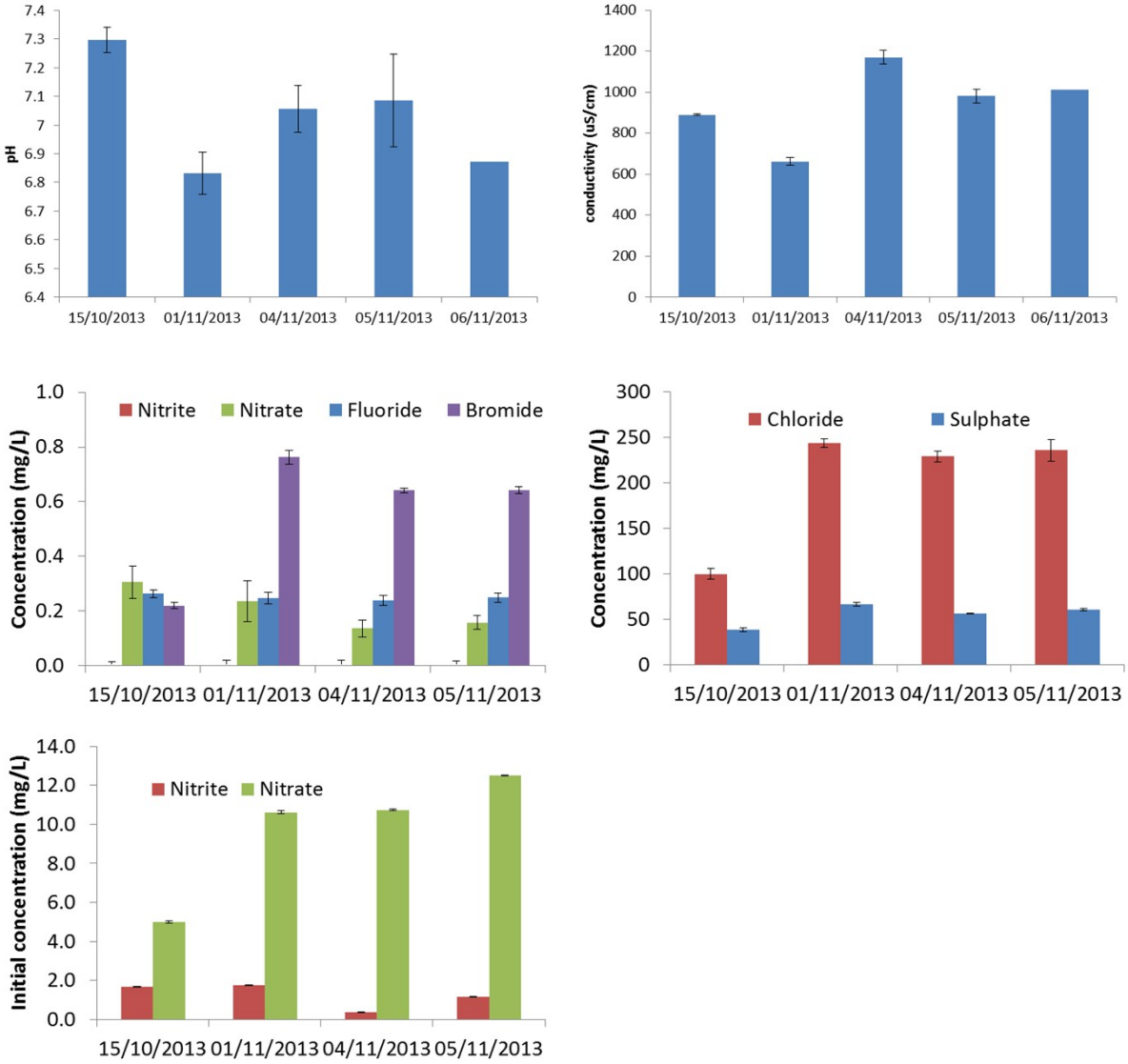

Figure SI-3. Average values of monitored parameters with standard deviations shown as error bars. Nitrate and nitrate values at the time of spiking (t = 0) are given in the bottom graph, whereas the other nitrate and nitrite values are the average of remaining measurements at other times when the levels were not changing.

Argument for small Ag particles

spICPMS detects Ag mass, not size. It should therefore be considered that enough dissolved Ag may accumulate on a WWT floc to appear as a very small particle during spICPMS measurements. The following calculation shows that this is unlikely. A typical adsorption site density for sludge particles is 2.4 x 10^{-3} mol g^{-1} [1] whereas the smallest detectable mass of Ag in a particle in experiment 1 was 8 x 10^{-18} g. The density of the sludge particles used in these experiments was measured using a pycnometer and found to be 1.002 g cm^{-3}. The minimum spherical diameter necessary to accommodate enough Ag mass to be detected as a 10 nm Ag nanoparticle in spICP-MS can thus be calculated to 88 µm. The spray chamber acts like a filter that removes droplets and particles that are larger than a few µm, although it does not have any sharp cut off value[2]. Most or all suspended solids

potentially carrying a high enough load of adsorbed dissolved Ag to be detected as a particle are therefore removed.

References

1. J. M. Wang, C.P. Huang, H. E. Allen, Surface physical-chemical characteristics of sludge particulates, *Water Environ. Res.*, 2000, **72**, 545-553.

2. L. Ebdon, M. Foulkes, K. Sutton, Slurry nebulization in plasmas, *J. of anal. at spectrom.*, 1997, **12**, 213-229.