

## Hybrid Multispectral Analysis (HMA): Innovative technology for continuously monitoring the biogeochemistry of urban waterways

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Hybrid Multispectral Analysis (HMA) uses a fiber optic spectrometer to analyze source and waste waters for multiple parameters. Hybrid refers to the HMA capability of measuring fluorescence and absorption as well as scattering to produce a rich array of optical data. No chemicals are required in HMA analysis. The optical information is then used to correct for artifacts such as turbidity and signal overlap before calculating concentrations based on laboratory calibrations performed in a clean water matrix. HMA data quality is maintained over time with automated cleaning and correction protocols. The HMA menu for source water includes TOC, nitrate, chlorophylls, turbidity, biochemical oxygen demand (BOD), total suspended solids (TSS), color, *E. coli* bacteria, fluorescent dissolved organic matter (FDOM) and other water quality parameters. Each value is displayed on a graphical web-user interface once every 2-3 minutes depending on the number of measurements in the menu. In this paper HMA data will be compared for several urban-impacted waterways including a small creek in Corvallis Oregon (Oak Creek) and a river-estuary in Sydney Australia (Parramatta River). The biogeochemistry of these urban streams will be compared to the relatively pristine, mountain-fed Santiam River in coastal Oregon. The high-resolution data from HMA allows details of important inter-parameter relationships to be examined in detail for the first time.

## Abiotic reactions of nitrite during microbial Fe(II) oxidation and their influence on cell-encrustation of nitrate-reducers

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Anoxic, nitrate-reducing bacteria are widespread in soils and sediments. They use nitrate ( $\text{NO}_3^-$ ) and the following intermediates ( $\text{NO}_2^-$ ,  $\text{NO}$  and  $\text{N}_2\text{O}$ ) as electron acceptors. In addition to heterotrophic denitrifiers, nitrate-reducers have been isolated which were suggested to couple nitrate reduction to the oxidation of Fe(II). Recently, however, it has been questioned whether the observed Fe(II) oxidation is completely enzymatic or whether it is at least partly due to an abiotic reaction between Fe(II) and the reactive N-species formed during mixotrophic growth [1,2,3]. Here we present data that demonstrates that  $\text{NO}_2^-$  is able to oxidize Fe(II) under pH-neutral and particularly under acidic conditions at high rates. Fe(II) analysis using sulfamic acid instead of HCl prevents the abiotic reaction of  $\text{NO}_2^-$  and Fe(II) during acidic extraction and yields correct Fe(II)/Fe(III) values. To evaluate the role of bacterially produced nitrite in Fe(II) oxidation, we compared two strains that were isolated as nitrate-dependent Fe(II)-oxidizers [1,2] with two heterotrophic nitrate-reducers (*Paracoccus denitrificans* ATCC 19367 & 1222) in their ability to oxidize ferrous iron and the formation of Fe(III) mineral crusts around the cells. All four tested strains oxidized Fe(II) and using SEM/TEM we observed heavy encrustation of all strains. However, the shape, crystallinity and localization of minerals inside and outside the cell varied distinctly between the strains. Applying fluorescent lectins in the CLSM, we also observed a significant production of exopolymeric substances, maybe as a protection mechanism against high Fe(II) concentrations. Our observations suggest that cell encrustation is a side effect caused by abiotic Fe(II) oxidation by nitrite during heterotrophic denitrification.

[1] Klueglein & Kappler (2013) *Geobiology* **11**, 180-190. [2] Weber *et al.* (2006) *Appl. Environ. Microbiol.* **72**, 686-694. [3] Kopf, Henny & Newman (2013) *Environ. Sci. Technol.* in press