

## Microbially influenced corrosion: Fe(0) as electron donor in freshwater ecosystems

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Iron rarely occurs in its elemental form naturally, however, steel constructions provide a common anthropogenic source in freshwater ecosystems. The oxidation of metallic iron leads to material deterioration posing environmental and economic risks. Fe(0) corrosion with O<sub>2</sub> as oxidant is mainly an abiotic process. In contrast, under anoxic conditions, microbial catalysis enables Fe(0) oxidation with weaker electron acceptors. Furthermore, Fe(0) represents a favorable electron donor for anaerobic respiration processes. We set out to investigate microbially influenced corrosion (MIC) in German inland waterways, combining field studies and enrichment cultures, aiming to determine key processes and key microorganisms. In-situ microsensor profiling revealed steep gradients of O<sub>2</sub>, redox potential, and pH within rust tubercles on sheet piles. Alkaline pH values (>9) indicated electrochemical reduction of O<sub>2</sub> on the outside. Inside, anoxic conditions prevailed with highly negative redox potentials (<-400 mV vs. SHE). Determination of bacterial gene copy numbers and sequencing of 16S amplicons suggested a densely populated tubercle with a phylogenetically and metabolically diverse microbial community. Among anaerobic metabolisms, the dissimilatory reduction of S compounds appeared to be most important with *Desulfovibrio* spp. being most abundant. In addition, incubations of corrosion scales from field sites were performed with different terminal electron acceptors (nitrate, sulfate, CO<sub>2</sub>) testing steel vs. H<sub>2</sub> as electron donor and auto- vs. heterotrophic (plus acetate) growth. Under sulfate reducing conditions, representatives of the Desulfocapsaceae dominated autotrophic steel incubations, while *Desulfovibrio* spp. were prevailing in heterotrophic steel incubations corresponding to field samples. Incubations with H<sub>2</sub> showed the dominance of *Desulfomicrobium* sp. and acetogenic bacteria affiliated to the genus *Acetobacterium*. Metaproteomic analysis performed on enrichment cultures identified enzymes involved in dissimilatory sulfate reduction such as DsrA and DsrB. Moreover, CytC3 and 4Fe-4S ferredoxin were detected being potentially involved in electron transport. Overall, we could demonstrate that sulfate reducing bacteria play a decisive role in steel corrosion in freshwater ecosystems. Further exploration of the overexpressed proteins would help us to identify marker proteins involved in MIC and metabolic pathway mapping of the identified enzymes to obtain an overview of the cellular processes.