1 **Anaerobic microbial manganese oxidation and reduction: a critical review**

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15   Anaerobic microbial manganese oxidation and reduction: a critical review

16   Manganese is a vital heavy metal abundant in terrestrial and aquatic environments.

17   Anaerobic manganese redox reactions mediated by microorganisms has been

18   recognized for a long time, which promote elements mobility and bioavailability in the

19   environment. Biological anaerobic redox of manganese serves two reactions, including

20   Mn(II) oxidation and Mn(IV) reduction. This review provides a comprehensive analysis

21   of manganese redox cycles in the environment, closely related to greenhouse gas

22   mitigation, the fate of nutrients, microbial bioremediation, and global biogeochemical

23   cycle, including nitrogen, sulfur, and carbon. The oxidation and reduction of manganese

24   occur cyclically and simultaneously in the environment. Anaerobic reduction of Mn(IV)

25   receives electrons from methane, ammonium and sulfide, while Mn(II) can function as

26   an electron source for manganese-oxidizing microorganisms for autotrophic

27   denitrification and photosynthesis. The anaerobic redox transition between Mn(II) and

28   Mn(IV) promotes a dynamic biogeochemical cycle coupled to microorganisms in water,

29   soil and sediment environments. The discussion of reaction mechanisms,

30   microorganism diversity, environmental influence bioremediation and application

31   identify the research gaps for future investigation, which provides promising

32   opportunities for further development of biotechnological applications to remediate

33   contaminated environments.

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1. Introduction

Manganese (Mn) is ranked fifth in the metal abundance in the earth crust, which has long

been recognized as an essential element for the life and environment with significant impacts

on the global biogeochemical cycle (Bjørklund et al. 2017). Divalent manganese (Mn(II)) and

tetravalent manganic oxide (Mn(IV)) serve as a reductant and an oxidant, respectively,

coupled to microorganisms that persist in marine and freshwater sediments and soils to

promote the complex network of biochemical interactions, including the tight interplay of

biotic and abiotic reactions, especially under anaerobic condition (Millero et al. 1987, Lovley

et al. 1988, Lovley 1991). Anaerobic biological Mn(II) oxidation and Mn(IV) reduction are

generally detected in environments rich in organic compounds and microorganisms.

The redox transition between the Mn(II) and Mn(IV) is closely connected to the

various biological processes. Mn(II) plays the role of reductant in anaerobic oxidation

reactions, providing electrons for various biochemical processes, including denitrification and

anaerobic photosynthesis (Su et al. 2015a, Su et al. 2015b, Daye et al. 2019). Mn(IV) exists

primarily as insoluble, solid-phase minerals in oxidation states. Mn(IV) oxide has been

demonstrated to oxidize diverse compounds, including organic matters, methane, ammonium

and sulfide, mediated by Mn(IV)-reducing bacteria (Table 1) (Ehrlich 1987, Myers et al.

1988, Thamdrup et al. 1993, Schink et al. 2006, Torres et al. 2014).

Microbial manganese redox reactions are critical for the environment, such as the

evolution of photosynthesis, geochemical transformation, degradation of organic matter and

mobilization or immobilization of various contaminants. Manganese bicarbonate can function

as an electron source for anoxygenic photosynthesis in the ancient world, considered the

precursor to oxygenic photosynthesis by producing oxygenic on the early earth (Daye et al.

2019, Chernev et al. 2020). The manganese redox cycle can mitigate methane emission,

which is a greenhouse gas causing global warming. The redox transition between the Mn(II)

62 and Mn(IV) can also remove active nitrogen, ammonium, nitrate and nitrite, from terrestrial

63 and aquatic environments (Burdige et al. 1983, Ehrlich 1987, Myers et al. 1988, Daye et al.

64 2019, Liu et al. 2019b). Compared to chemically synthetic manganese oxide, biologically

65 produced manganese oxide (BioMnOx) has specific characteristics, such as high specific

66 surface areas and high catalytic reactivity (Villalobos et al. 2006). BioMnOx is proved to

67 oxidize complex organic matters, including humic and fulvic acids (Sunda et al. 1994), 17 α -

68 Ethinglestradiol (Kim et al. 2012), diclofenac (Forrez et al. 2010), and Polychlorinated

69 Biphenyls (PCBs) (Pizzigallo et al. 2004), which can provide the possibility to apply biogenic

70 manganese oxides to bioremediation of organic pollutants.

71   This review discusses the intricate biogeochemical of microbe-mediated manganese

72 oxidation and reduction in anaerobic environments to identify the research gaps and potential

73 ecological application for future investigation. We introduced anaerobic microbial manganese

74 oxidation, including light-driven manganese oxidation and nitrate-dependent manganese

75 oxidation. (section 2). We then provided an overview on manganese reduction mediated by

76 microorganisms coupled with organic carbon oxidation, methane oxidation, ammonium

77 oxidation and sulfide oxidation (section 3). After that, we provided a comprehensive review

78 of the significance of the biochemical role of manganese in the environment (section 4). In

79 addition, we discussed the research gap in the investigation of manganese in the environment

80 (section 5). During these discussions, we identified research and development opportunities,

81 including functional mechanisms, manganese cycle applied in biological technology and

82 potential new application.

83 **2 Anaerobic Microbial Manganese Oxidation**

84 *2.1 Nitrate-dependent Manganese Oxidation (NDMO)*

85 The reduction of nitrate coupled to Mn(II) oxidation was observed under the anoxic

86 circumstance mediated by nitrate-reducing microorganisms for a long time (Nealson et al.

87 1992). Before 1988, the environmental data, including the distributions of Mn(II), NO_3^- and

88 MnO_2 in sediments where O_2 is absent, led many investigators to speculate that Mn(II) could

89 theoretically reduce NO_3^- coupled with microorganisms (Aller 1990, Nealson et al. 1992,

90 Hulth et al. 1999). Recent studies on nitrate and nitrite reduction mediated by Mn(II)

91 oxidation, indicate possible mechanisms and responsible microorganisms (Figure 1) (Su et al.

92 2016a, Su et al. 2016b).

93   *Acinetobacter sp.* SZ28 and *Pseudomonas sp.* SZF15 are autotrophic denitrification

94 bacteria, which were demonstrated to utilize inorganic carbon as carbon source, nitrate and

95 nitrite as electrons acceptors for Mn(II) oxidation, converting nitrate to nitrite and then to

96 nitrogen (Su et al. 2015a, Su et al. 2016a, Su et al. 2016b). The *napA* gene and the *nirS* genes

97 were detected in these two bacteria, encoding periplasmic nitrate reductase and nitrite

98 reductase, respectively (Bell et al. 1990). These two enzymes are essential for the nitrate and

99 nitrite reducing processes (Su et al. 2015a, Su et al. 2015b, Su et al. 2019a). With the

100 recognition of *napA* genes and nitrate reductase, the first step of the NDMO process is to

101 convert nitrate to nitrite (Bedzyk et al. 1999, Smith et al. 2007, Sparacino-Watkins et al.

102 2014). The nitrite reductase, encoded by *nirS*, can also be observed, which reduces nitrite to

103 nitric oxide (Yamanaka et al. 1961, Sparacino-Watkins et al. 2014). So, the bacteria have

104 capacity to reduce nitrite. Nitric oxide reductase (*NorB or NorC)* and nitrous oxide reductase

105 (*Nos*), which are also essential genes for autotrophic denitrification (Liu et al. 2019a), has not

106 been investigated yet. The final products of the NDMO process are nitrogen with a trace

107 amount of N_2O that may be an intermediate product. The metabolic pathway in manganese-

108 oxidizing microorganisms and manganese oxidization fate have not been detected.

109   The bioreactor indicates that nitrate was reduced to nitrogen coupled to microbial

110 oxidation of Mn(II) (Hulth et al. 1999). Several factors significantly influence the nitrate

111   removal rate of the anaerobic biological Mn(II) oxidation process, including reactor

112   configuration, pH, and temperature. The optimal conditions for *Acinetobacter sp.* SZ28

113   applied in batch reactors are initial Mn(II) concentration of 143.56 mg/L, C/N ratio of 6.82,

114   initial pH of 5.17 and temperature of 34.26℃ with a removal rate of 0.063mg NO_3^-N/L/h,

115   while as the bacteria in moving bed biofilm reactors, the nitrate removal efficiency can reach

116   77.44% under pH of 5.21 (Su et al. 2015b, Su et al. 2016a). In the batch reactor, the nitrite

117   shown an increase from 0.04mg/L to 0.1mg/L, and then decreased to 0.05mg/L (Su et al.

118   2015b). For the optimal pH, Hulth et al. (1999) suggested that Mn(II) oxidation is

119   thermodynamically favorable in relative high pH conditions. However, the microbial

120   reactions are affected by various factors, such as characteristics and activity of

121   microorganisms, temperature, and coexisting microorganisms. In addition, the Mn(II) will

122   deposit under high pH conditions, which is hard utilized by microorganisms. The mixture of

123   Fe(II) and Mn(II) also shows a significant removal efficiency of nitrate and nitrite in both

124   batch and moving bed biofilm reactor with the optimal molar ratio of Mn(II)/Fe(II) of 7:3 and

125   3:7 (Su et al. 2017a, Su et al. 2017b, Luo et al. 2019). The nitrite can be detected in the

126   bioreactor, but bacteria were able to reduce the nitrite completely (Su et al. 2017b).

127   Nitrate, nitrite and manganese are common contaminants in groundwater due to

128   industrial discharge, agriculture, and urban effluent, threatening human health (Sarioglu et al.

129   2012). With the research on the nitrate-reducing bacteria and Mn(II) in batch and bed moving

130   biofilm reactors, the NDMO process may have effects on the manganese transformation in

131   groundwater.

132   *2.2 Light-driven Anaerobic Microbial Manganese Oxidation*

133   Manganese oxidation can be driven by light energy via the photosynthesis of microorganisms.

134   Light-driven anaerobic microbial manganese oxidation has been demonstrated to exist in the

135 ancient environment (Planavsky et al. 2014, Chernev et al. 2020). At an early stage of earth

136 evolution, ancient photosynthetic activities can form Mn-oxide nanoparticles of the birnessite

137 type by microbial Mn(II) oxidation. The Mn-oxide nanoparticles, formed by ancient

138 photosystem II (PSII) and evolved into the Mn_4CaO_5 cluster of today's PSII, are essential for

139 water oxidation of photosynthetic microorganisms to shape the biosphere and atmosphere,

140 and geosphere (Chernev et al. 2020). Mn(II) oxidation by anaerobic microbial photosynthesis

141 is a critical step in the evolution of aerobic metabolism and complex life, which changed the

142 face of the earth (Dismukes et al. 2001).

143   Daye et al. (2019) proposed the existence of light-driven Mn(II) oxidation by today's

144 photosynthetic activity of microorganisms. *Chlorobium limicola* coupled to *Geobacter lovleyi*

145 showed the ability to oxidize Mn(II) anaerobically. Light-dependent manganese oxidation

146 was only observed in the co-culture of *Chlorobium limicola* with *Geobacter lovleyi*. By

147 contrast, manganese oxidation has not been detected in the pure cultures of *Chlorobium*

148 *limicola*. *Chlorobium limicola* is green sulfur bacteria that use photosystem l (PSl) for

149 photosynthesis. Bacteriochlorophyll is the main component for conducting photosynthesis

150 without the production of oxygen, receiving light energy, and transferring it to Fenna-

151 Matthews-Olson (FMO)-proteins (Figure 2a) (Ashraf 2014, Keenleyside 2019, Chen et al.

152 2020). FMO provide the energy for the reaction center, which receives the energy for electron

153 transfer (Figure 2b) (Van Niel 1932, Oh-oka et al. 2013). The green sulfur bacteria typically

154 utilized sulfur as electron donors providing electrons for carbon dioxide fixation (Chen et al.

155 2020). As green sulfur bacteria mainly use sulfide ions as electron donors, Mn(II) oxidation

156 can only occur as sulfide concentration under 0.2mM (Daye et al. 2019). *Geobacter* sp., an

157 anaerobic electrogenic bacteria species that achieve electron exchange by extracellular

158 electron transfer, can also oxide metals (Figure 2c) (Butler et al. 2010, Bonanni et al. 2012).

159 Therefore, electron transfer may occur between these two organisms. Dolomite is formed on

160 the surface of *Chlorobium limicola.* cells and around extracellular vesicles. The amount of

161 oxidized manganese in the biofilms increased with time, while it was not found in the biofilm

162 cultured in the dark (Daye et al. 2019). However, the interspecies interactions between

163 *Chlorobium sp.* and *Geobacter sp.* are unknown currently, and mechanisms of light-driven

164 manganese oxidation bacteria remain to be identified.

165   The light-drive anaerobic oxidized manganese process exists in water bodies and

166 sedimentary photic zones, coupled with the carbon and oxygen redox cycle in Archaean and

167 modern ecosystems. Manganese oxide in sediment and rock can provide evidence for the

168 timing of the origin of oxygenic photosynthesis, which is significant to the biological origin

169 (Daye et al. 2019).

170 **3. Anaerobic Microbial Manganese Reduction**

171 *3.1 Manganese Reduction Coupled to Organic Carbon Oxidation*

172 In recent years, the role of manganese reduction in promoting the oxidation of organic carbon

173 has received increasing attention. Mn(IV)-dependent anaerobic oxidation of organic carbon

174 has been inferred from geochemical evidence in freshwater (Lovley et al. 1988) and marine

175 (Vandieken et al. 2014) sediments. In the manganese-rich environment, manganese reduction

176 contributes 25% to approximately 100% of anaerobic carbon oxidation (Aller 1990, Canfield

177 et al. 1993b, Thamdrup 2000, Vandieken et al. 2006, Nickel et al. 2008). Mn(IV)-reducing

178 bacteria has been identified to mediate oxidation of organic electron donors, which can use

179 complex dissolved Mn(IV) as electron acceptor (Vandieken et al. 2012, Vandieken et al.

180 2014). The organic electron donors used by Mn(IV) reducer include acetate and lactate

181 (Canfield et al. 1993a, Vandieken et al. 2014). Acetate is one of the primordial organic carbon

182 substrates for microorganisms (Russell et al. 2004). Mn(IV) reduction is associated with

183 acetate metabolism and microorganism growth with Mn(II) and carbon dioxide products. The

184   acetate is consumed by Mn(IV) reducer for energy generation, and this capability has been

185   demonstrated for different microorganisms, including *Colwellia*, *Oceanospirilaceae*, and

186   *Arcobacter*, in anoxic environments (Vandieken et al. 2012).

187   Mn(III) is a newly identified oxidant that may be formed by Mn(IV) oxide reduction

188   and Mn(II) oxidation, which oxidize acetate for supporting anaerobic bacteria respiration,

189   dominated by *Shewanella* and *Dechloromonas* (Szeinbaum et al. 2014, Szeinbaum et al.

190   2020). This finding provides a new biogeochemical link between carbon and manganese

191   cycles and fills the gap of two successive one-electron transfer steps of Mn(IV) to Mn(II).

192   Thus, Mn(IV) is reduced to Mn(III), and Mn(III) is the terminal electron acceptor linked to

193   anaerobic microbial respiration (Szeinbaum et al. 2014, Szeinbaum et al. 2017, Szeinbaum et

194   al. 2020).

195   Anaerobic Mn(IV)/(III) reduction coupled to organic carbon oxidation have been

196   demonstrated to be responsible for 90% of total organic carbon oxidation in the Danish

197   coastal (Canfield et al. 1993a), 13%-35% in the Black Sea (Thamdrup et al. 2000), and 57%

198   in Ulleung Basin (Hyun et al. 2017). The bioturbation drives manganese cycling coupled with

199   nutrient circulation and regeneration in an anoxic environment, an important step in energy

200   and carbon conversion and biogeochemical cycling.

201   *3.2 Manganese Reduction Coupled to Methane Oxidation*

202   Methane is the second potent greenhouse gas next to carbon dioxide. The radiative forcing

203   produced per molecule of methane is greater than that of carbon dioxide, and the global

204   warming potential value of methane is 84 in the 20-year period (Boucher et al. 2009, Stocker

205   et al. 2013). Anaerobic oxidation of methane (AOM) can significantly mitigate methane

206   emissions and global warming (Valentine et al. 2000, Sivan et al. 2011, Ding et al. 2015).

207   Moreover, the anaerobic methanotrophic archaea (ANME) can conduct AOM coupled

208   with sulfate, nitrate, iron (ferrihydrite) and manganese (birnessite) reduction (Beal et al. 2009,

209   Cai et al. 2018, Xu et al. 2018, Su et al. 2019b, Nie et al. 2020). ANME belonging to the

210   archaeal family *Methanoperedenaceae* (formerly known as ANME-2d) has been identified to

211   mediating AOM coupled to metal oxides (Fe(III), Mn(IV)) reduction in freshwater systems

212   such as lake and wetland (Beal et al. 2009, Torres et al. 2014, Ettwig et al. 2016, Liu et al.

213   2019b, Nie et al. 2020). Two novel members of the *Methanoperedenaceae* named *Candidatus*

214   *Methanoperdens manganicus* and *Candidatus Methanoperedens manganireducens* were

215   identified to utilize Mn(IV) oxides as an electron acceptor (Leu et al. 2020). The

216   stoichiometry assessment of the Mn(IV)-dependent AOM shows Mn(IV)/reactant of methane

217   ratio of 4:1. The evidence indicated that *Ca. M manganicus* and *Ca. M. manganireducents*

218   showed a clear preference for utilizing manganese as electron acceptors compared with other

219   oxidants. *Ca. M. manganicus* and *Ca. M. manganireducents* reveal different electron transport

220   mechanisms (Leu et al. 2020). The multi-heme c-type cytochromes mediate the electron

221   transfer from methane oxidation to Mn(IV) oxides. In *Ca. M. manganicus*, four out of six

222   multi-heme c-type cytochromes are highly expressed (Figure 3a), while in *Ca.M.*

223   *manganireducents*, a b-type cytochrome and a 6-heme MHC were highly expressed (Figure

224   3b) (Su et al. 2019a, Leu et al. 2020). This new finding indicates that *Ca. M. manganicus* and

225   *Ca. M. manganireducents* can couple AOM to Mn(IV) reduction independently. Manganese-

226   rich environments, such as margins of black-shale, possibly provide suitable habitats for these

227   two archaea, potentially impacting the global carbon and manganese cycles.

228   *3.3 Manganese Reduction Coupled to Ammonium Oxidation*

229   The anaerobic microbial ammonium oxidation coupled to reducing manganese in the

230   environment has been recognized for a long time (Luther III et al. 1997, Aller et al. 1998).

231 This process occurs in anoxic, rich in organic matters and manganese environments such as

232 marine and freshwater sediment (Aller et al. 1998, Bartlett et al. 2008, Fernandes et al. 2015).

233 From the thermodynamics perspective, Mn(IV) reduction coupled to ammonium oxidation

234 theoretically results in converting NH_4^+ to NO_3^- and NO_2^-, or in the most thermodynamically

235 favorable option to N_2 (Mortimer et al. 2004, Anschutz et al. 2005, Lin et al. 2014, Torres et

236 al. 2014, Fernandes et al. 2015). In freshwater sediment bioreactors, nanoscale oxides of

237 manganese can act as an electron acceptor in the biological oxidation of NH_4^+. Under the

238 optimal condition of pH at 7 and temperature of 25℃, the maximum removal rate of NH_4^+

239 reach (126 ± 11.3 mg/L/d) (Swathi et al. 2017). Both NO_3^- and NO_2^- are end products of the

240 process. The microorganisms mediating the reduction of nanoscale oxides of manganese

241 coupled to oxidation of NH_4^+ need further investigation.

242 *3.4 Manganese Reduction Coupled to Sulfide Oxidation*

243 Manganese reduction is believed to be associated with sulfide-oxidizing bacteria. In the

244 anaerobic aquatic system, Mn(IV) oxides can oxidize sulfide biotically, leading to the

245 formation of elemental sulfur (Burdige et al. 1986), sulfate (Aller et al. 1998) and small

246 amounts of thiosulfate (Herszage et al. 2003). Burdige et al. (1986) proposed that sulfide was

247 oxidized to sulfur coupled to anaerobic manganese reduction, whereas sulfate was the

248 dominant product with traces of thiosulfate in other studies (Aller et al. 1988, Herszage et al.

249 2003). The sulfide oxidation products change with the environmental pH. At low pH, the

250 sulfide is oxidized to sulfate, while, at near-neutral pH, the main product of sulfide reduction

251 is elemental sulfur. The Mn(IV) can be reduced to the Mn(II) in the sulfide oxidation process.

252 The current research reveals that a single strain named *Sulfurimonas marisnigri* was

253 successfully isolated from the Black Sea. The species can mediate the sulfide oxidation

254 coupled with Mn(IV) reduction with sulfide oxidized completely to sulfate (Henkel et al.

255 2019). The genus *Sulfurimonas* belongs to the *Epsilonbacteraeota,* abundant in marine

256   sediments (Han et al. 2015, Wang et al. 2021). With abundance of *Sulfurimonas,* the

257   biological anaerobic sulfide oxidation coupled with manganese reduction potentially leads to

258   a tight interaction between manganese and biogeochemical sulfur cycles (King 1990,

259   Herszage et al. 2003).

260   **4. Environmental Significance**

261   *4.1 Biogeochemical Significance for Greenhouse Gases mitigation*

262   Methane is a more potent greenhouse gas than carbon dioxide, estimated to contribute about

263   20% of post-industrial global warming (Knittel et al. 2009, Stocker et al. 2013, Cai et al.

264   2016, Liu et al. 2021). Anaerobic methane oxidation is essential for controlling global

265   methane emissions, which consume over 90% methane in the environment (Knittel et al.

266   2009). AOM coupled to Mn(IV) is a significant branch of anaerobic methane oxidation,

267   commonly occurring in marine and freshwater sediment. During the Proterozoic, the methane

268   flux to the atmosphere was approximate 1000 to 10000 Tg/year, and manganese and iron-

269   depend AOM are estimated to oxidize the entire early global methane flux (Pavlov et al.

270   2003). Meanwhile, the Mn(IV) reduction has been demonstrated to dominate the AOM in Mn

271   oxide-rich places (Canfield et al. 1993a). The manganese can be oxidized and reduced 100 to

272   300 times (Canfield et al. 1993a). Therefore, even only a tiny part of manganese in the

273   environment, a large amount of methane still can be oxidized, contributing to the global

274   mitigation of methane emission.

275   *4.2 Impact of Manganese Transformation on Biogeochemical Cycles*

276   In anaerobic environments, the microbial manganese oxidation and reduction processes

277   motivate the biogeochemical manganese cycle. These processes occur cyclically and

278   simultaneously and are closely related to nitrogen, carbon, and sulfur cycles (Bender et al.

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279   1989, Straub et al. 1996, Luther III et al. 1997). In the manganese-rich environment, Mn(IV)

280   oxides are reduced to Mn(II) by ammonium forming nitrate or nitrite. Mn(IV) reduction is a

281   thermodynamically favorable reaction with a high possibility of occurrence (Hulth et al.

282   1999). The nitrification process occurs with the denitrification process simultaneously in the

283   environment (Luther III et al. 1997, Hulth et al. 1999, Tan et al. 2021). The Mn(II), nitrate,

284   and nitrite may never accumulate in the environment due to the nitrite-dependent Mn(II)

285   oxidation process. The interaction between manganese and nitrogen species can motivate the

286   environmental nitrogen cycle (Figure 4).

287   As to the sulfur cycle, the manganese redox cycle may be closely tied to the sulfur

288   cycle mediated by microorganisms (Liu et al. 2020). The anaerobic Mn(IV) reduction can

289   contribute to sulfide oxidation with products of sulfur or sulfate (Herszage et al. 2003). The

290   sulfate-reducing bacteria coupled to the sulfate reduction process lead to sulfide formation

291   (Burdige et al. 1986). Compared to iron, manganese has higher environmental turnover rates,

292   indicating the importance of sulfur and manganese cycles (Figure 4) (Thamdrup et al. 1994).

293   The manganese redox process also promotes the carbon cycle by mediating the anaerobic

294   microbial methane oxidation, in which the products are carbon dioxide and water.

295   The nitrogen cycle has been accelerated by the massive production and industrial use

296   of artificial nitrogen fertilizer worldwide (Gruber et al. 2008). Human activities such as

297   burning fossil fuels and industrial carbon emissions also altered the carbon cycle. (Solomon et

298   al. 2007). The cycles of elements did not occur in isolation. For instance, the nitrogen in the

299   atmosphere deposited on the ground is utilized by plants, stimulating productivity and

300   enhancing carbon dioxide uptake from the atmosphere (Schimel et al. 2001). With humans

301   producing a large impact on biochemical element cycles, the microorganisms try to produce a

302   new steady state in nature. The research on manganese mediating the bioprocesses provides

303   opportunities to investigate the new steady state, which has the potential to address the issue

304   of climate. Given the various related environmental reactions, the reactions are spatially

305   overlapped, involving different microorganism respiration (Thamdrup et al. 1994). The

306   current research can only reveal the part of these cycles. The unconfirmed processes in the

307   microbial manganese redox web still need to be investigated for further research.

308   *4.3 Bioremediation*

309   The contaminated environment caused by industrial and human activities threatens human

310   health. Bioremediation is a branch of biotechnology that employ microorganisms to remove

311   harmful contaminants from the environment (Vidali 2001). Biological manganese redox

312   reactions provide opportunities for bioremediating contaminated soil and water. Manganese

313   redox reactions mediated by microorganisms has a strong potential of removing organic

314   pollutants in anaerobic environment.

315   The manganese oxides formed by anaerobic Mn(IV) reduction coupled to manganese-

316   reducing microorganisms shows a capacity of removing different kinds of organic

317   micropollutants. Compared to the chemically produced manganese oxides, biologically

318   produced manganese oxides (BioMnOx) have high specific surface areas and high catalytic

319   reactivity, leading to high oxidation capability (Forrez et al. 2010). Diclofenac is a

320   nonsteroidal anti-inflammatory for treating pain and inflammatory diseases, toxic to several

321   aquatic organisms (Lonappan et al. 2016). The diclofenac oxidation rate is consistent with the

322   amount of BioMnOx, and at the neutral pH, the BioMnOx reduction was ten times faster than

323   chemical manganese oxides. As BioMnOx combined with biogenic silver nanoparticles, the

324   diclofenac oxidation is more rapid (Meerburg et al. 2012). 17^α-Ethinylestradiol and

325   polychlorinated biphenyls are persistent organic pollutants, widespread problems in the

326   environment due to their threats to human health and concentrating in biota (Aris et al. 2014).

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327 BioMnOx is capable of removing 17α-Ethinglestradiol and polychlorinated biphenyls from

328 the water system (Pizzigallo et al. 2004, Kim et al. 2012).

329   The mitigation of organic pollution is hard to implement due to technical difficulties

330 associated with monitoring these low-concentration pollutions , the high cost of widespread

331 installation of pollution treatment technologies and incomplete elimination. (Jobling et al.

332 2011, Owen et al. 2012, Verlicchi et al. 2012, Larcher et al. 2013, Mills et al. 2015; Wei et al.,

333 2020). The biological methods for water treatment are simple, economically attractive, and

334 well accepted by the public, which has been investigated efficient elimination of organic

335 matter (Crini et al. 2019). Mn-relate bioprocesses on organic pollution treatment provide an

336 important foundation for further studies into installing highly efficient, low cost, treating a

337 wide variety of pollutions technologies.

338 **5. Future Perspective**

339 *5.1 Exploring the Mechanisms of Manganese Redox Reaction*

340 The manganese redox reactions include many processes (denitrification, ammonia oxidation,

341 methane oxidation, sulfide oxidation, etc.), but the fundamental mechanisms and functional

342 microorganisms are unclear currently. Only a few microorganisms have been discovered,

343 such as manganese functions as an electron source for manganese-oxidizing microorganisms,

344 including *Acinetobacter sp.* SZ28 (Su et al. 2019b) and *Pseudomonas* sp. SZF15 (Su et al.

345 2017a) functions as an electron acceptor for manganese-reducing microorganisms, such as

346 *Candidatus Methanoperedens manganicus* and *Candidatus Methanoperedens*

347 *manganireducens* (Leu et al. 2020). In addition, key genes of functional microorganisms need

348 to be identified, which encode a massive number of proteins conducting these manganese

349 redox reactions. Identifying key genes and understanding the roles of these differentially

350 expressed proteins is needed to construct metabolic pathways for these reactions and indicate

351 different electron transfer pathways. Further investigations is required to identify active

352 functional microorganisms, characterize the specific genes and proteins, structure the

353 metabolic constructions and analyze electron transfer pathways. Mechanism research can

354 provide the foundation for future studies on the environmental significance of manganese.

355 *5.2 Interspecific Interaction*

356 Interspecific interactions are frequent in the environment, including metabolic interactions

357 (Ponomarova et al. 2015), interspecific transfer (Roy 1984, Maruyama et al. 1991, Walker et

358 al. 2009), quorum sensing (De Kievit et al. 2000, Miller et al. 2001, Ng et al. 2009), and

359 activation of silent genes (Wang et al. 1988, Avivi et al. 2004). In the reactors of sediment

360 incubation, the oxidized manganese could only be observed in the co-culture of *Arthrobacter*

361 sp. QXT-31 and *Sphingopyxis* sp. QXT-31, while no manganese oxide was detected in the

362 monoculture of these two bacteria. *boxA* gene in the *Arthrobacter* sp. encodes Mn(II)

363 oxidizing enzymes was known as bilirubin oxidase, which may only be activated by the stress

364 of *Sphinpoyxis*, as it sustained contact with the metabolically active *Sphingopyxis* sp. (Liang

365 et al. 2016). A similar interspecies interaction for Mn(II) oxidation also can be found between

366 *Corynebacterium* and *Chromobacterium* (Bromfield et al. 1950, Bromfield 1956). For light-

367 drive manganese oxidation, the reaction only occurred as *Chlorobium* sp. grew with

368 *Geobacter* sp. Manganese oxides can be observed on the surface of *Chlorobium* sp. (Daye et

369 al. 2019). The interaction among two or more microorganisms may promote the manganese

370 oxidation process. However, the interspecific interaction mechanism of light-driven

371 manganese oxidation is unclear, as the photosynthetic reaction cannot support enough energy

372 for direct manganese oxidation (Dismukes et al. 2001, Dasgupta et al. 2006).

373 The interaction of microorganisms can expand the network of microbial manganese

374 oxidation and reduction. Meanwhile, the interaction involves various chemical and biological

16

375   factors in the ecosystem, which promote the elemental cycle of the ecosystem. Further studies

376   need to focus on investigating mechanisms and unclear interspecific interaction on the

377   manganese in the environment.

378   *5.3 Geochemical Evidence for Manganese-mediated Methane Mitigation*

379   The environmental significance of manganese transformation has long been investigated.

380   Although the manganese transformation is demonstrated to contribute to methane mitigation,

381   the methane oxidation rate coupled with manganese has not been well quantified (Liu et al.

382   2019b). The manganese was not be investigated independently, which is commonly analyzed

383   with other heavy metal reductions (Canfield et al. 1993a). Significant efforts are needed to

384   detect the relationship between global methane mitigation and manganese reduction, such as

385   investigating methane and manganese concentration in regional scales, monitoring methane

386   and manganese flux, and modelling the methane mitigation coupled with manganese in

387   aquatic and terrestrial ecosystems. Nitrogen loss is a severe agriculture problem dominated by

388   nitrate (Van Kessel et al. 2009). The manganese redox promotes nitrate formation and

389   consumption in the ecosystem (Swathi et al. 2017), but the environmental impact of

390   manganese on nitrogen loss remains unclear. The in-situ experimental conclusions are

391   obtained from the laboratory under controlling different conditions, which provides deep

392   insight into the mechanism of manganese redox. However, reactions may be impacted by

393   various factors in the actual environment, such as changing temperatures, other

394   microorganisms, other substances in nature, etc.

395   *5.4 Potential for Practical Application*

396   Manganese redox cycle mediated by microorganisms can balance nitrogen, carbon, and sulfur

397   in the ecosystem, which may be utilized in the wastewater and groundwater treatment. The

398   traditional water treatment methods are physical, chemical, and both (Jorgensen et al. 2003,

399   An et al. 2005). Biological methods used in water treatment is highly efficient, low cost and

400   eco-friendly. The microorganisms have a high potential to be utilized in water treatment with

401   advantages. The pollution of nitrate in groundwater is a severe environmental problem

402   receiving concern from the public worldwide (Xue et al. 2016). Meanwhile, Mn oxide can be

403   used manganese-reducing microorganisms to reduce methane emission and remove NH_4^+-N

404   from the water (Camargo et al. 2006, Segarra et al. 2015).

405   Furthermore, biological Mn(IV) reduction can also be applied to cobalt recovery from

406   laterites (Newsome et al. 2020). Cobalt is an essential raw material in the industry vital for the

407   economies (Newsome et al. 2020). Cobalt mobility is closely associated with Mn-reducing

408   bacteria, which can be applied in cobalt and nickel industrial recovery with high efficiency

409   and eco-friendly (Newsome et al. 2020). The current methodologies recovering cobalt from

410   laterites using pressure acid leaching, heap leaching and or solvent extraction (Kursunoglu et

411   al. 2016, Oxley et al. 2016). A two-step process develops from the Mn-driven cobalt cycle for

412   the industrial laterites treatment process (Newsome et al. 2020). With manganese-reducing

413   microorganisms, cobalt is transformed to a more labile 'exchangeable' phase that could be

414   extracted using a simple acetic acid wash. The process generates less waste, and organic

415   substrates supplied to the microorganisms are environmentally friendly and potentially

416   sourced from waste carbon substrates (Newsome et al. 2020). Therefore, the biological

417   manganese redox can be applied to various industrial processes with a series of complex

418   reactions, including groundwater and wastewater treatment and cobalt and nickel recovery.

419   The current research only explores a small part of the application with the reactions. Further

420   studies on the application for biological manganese redox should provide more advanced

421   methodologies for industrial systems by building an eco-friendly engineering system with no

422   harmful emission and discharge.

6. Conclusion

Over the past half-century, recognizing anaerobic manganese microbial reduction and oxidation has been identified as a significant process. It is a long way to investigate the diversity, behavior, and physiology of microorganisms that mediate Mn(II) oxidation and Mn(IV) reduction. The environmental influence of manganese transformation has also been identified, associated with greenhouse gas mitigation, carbon storage and nutrient cycling. The increasing detection of new complex manganese redox reactions on biogeochemical cycles enables us to detect and unravel the competing and interdependent manganese cycle processes. The biogeochemical cycling of manganese is linked to the dynamic balance with biogeochemical cycling on the earth via carbon dioxide formation and sulfide, ammonia, and methane oxidation by Mn(IV)-reducing microorganisms, co-occurring with nitrate reduction by Mn(II)-oxidizing microorganisms. These advances provide the potential for manganese biotechnology applications. The geochemical importance and engineering application of manganese open various future research directions.

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Table 1

Table 1 Standard Gibbs free energy of manganese oxidation and reduction at pH=7

| Reaction	$\Delta G^{0'}$(kJ/mol)	Ref.
Oxidation		
$5Mn^{2+} + 2NO_3^- + 4H_2O \rightarrow 5MnO_2 + N_2 + 8H^+$	-14.35	(Swathi et al., 2017)
Reduction		
$CH_3COO^- + 4MnO_2 + 2HCO_3^- + 3H^+ \rightarrow 2MnCO_3 + 4H_2O$	-737	(Lovley & Phillips, 1988)
$CH_4 + 4MnO_2 + 7H^+ \rightarrow HCO_3^- + 4Mn^{2+} + 5H_2O$	-556.00	(Beal et al., 2009)
$4MnO_2 + NH_4^+ + 6H^+ \rightarrow 4Mn^{2+} + NO_3^- + 5H_2O$	-269.27	(Swathi et al., 2017)
$3MnO_2 + NH_4^+ + 4H^+ \rightarrow 3Mn^{2+} + NO_2^- + 4H_2O$	-195.14	(Swathi et al., 2017)
$3MnO_2 + 2NH_4^+ + 4H^+ \rightarrow 3Mn^{2+} + N_2 + 6H_2O$	-552.89	(Swathi et al., 2017)
$8H^+ + 4MnO_2 + FeS \rightarrow 4Mn^{2+} + SO_4^{2-} + Fe^{2+} + 4H_2O$	-592	(Hulth et al., 1999)
$3H^+ + MnO_2 + HS^- \rightarrow Mn^{2+} + S^0 + 2H_2O$	-136	(Hulth et al., 1999)
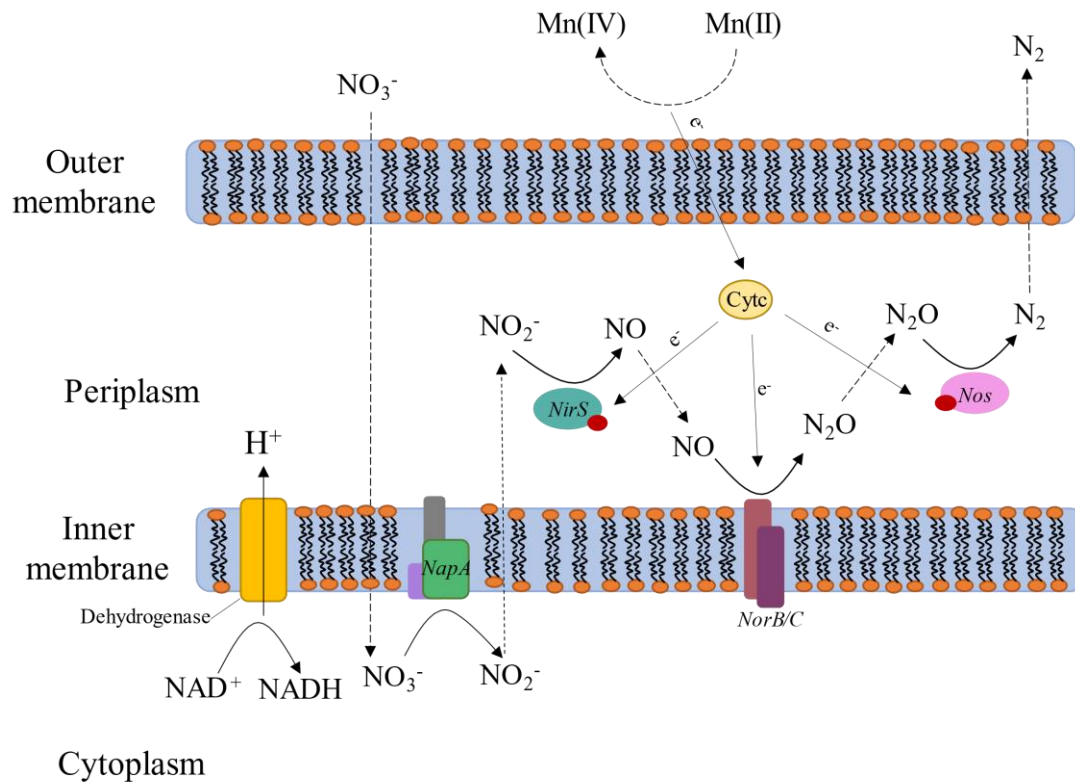
Figure 1

Figure 1The probable mechanisms of nitrate-dependent Mn(II) oxidation. Nitrate reductase (Nar) and nitrite reductase (Nir) reduce nitrate to nitrite and nitrite to nitric oxide, respectively. Nitric oxide reductase (Nor) and nitrous oxide reductase (Nos) reduce nitric oxide to nitrous oxide and nitrous oxide to nitrogen.
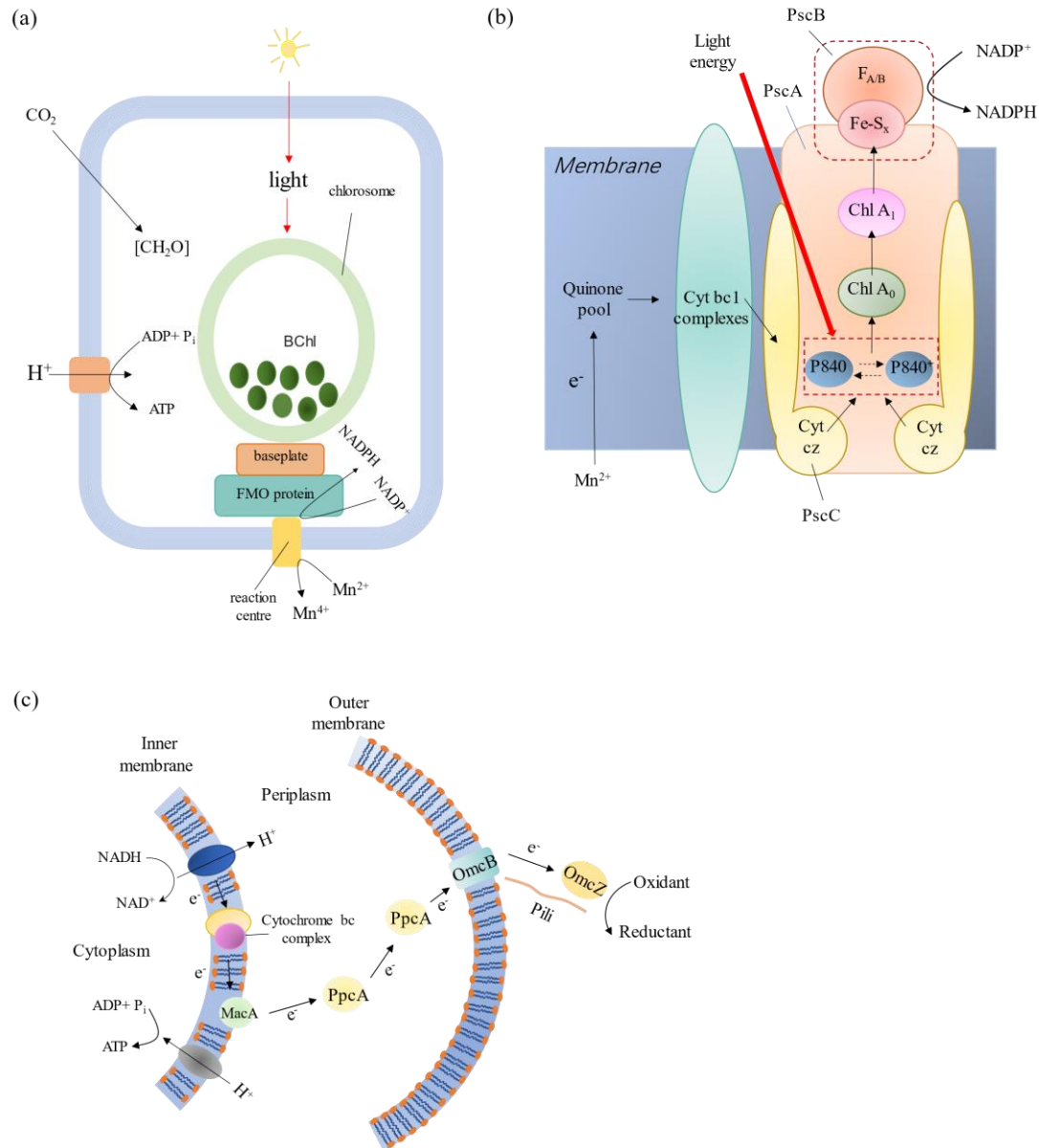
Figure 1 Photosynthesis of green sulfur bacteria and electron transfer in *Chlorobium sp*. and Geobacter sp.. (a) bacteriochlorophyll (Bchl) can absorb light and transform light into energy. Bchl transfers light energy to FMO protein which connects with reaction centers. (b) Electron transfer in the reaction center through the quinone pool to cytochrome bc1 and Cyt cz (cytochrome C553 and C551). P840 and P840+ is a special pair of BChl a in the reaction center. For the transformation of the pair of BChl a, P840+ is re-reduced by Cyt cz, and P840 provides electrons to the first Chl (A) and the second Chl(A0). The PscB is the stromal subunit of the reaction center, containing two 4Fe-4S, FeA and FeB, the terminal electron acceptor to promote NADP+ and NADPH transformation. (c) the electron-transport process from the inner membrane to extracellular compounds in *Geobacter sp*..

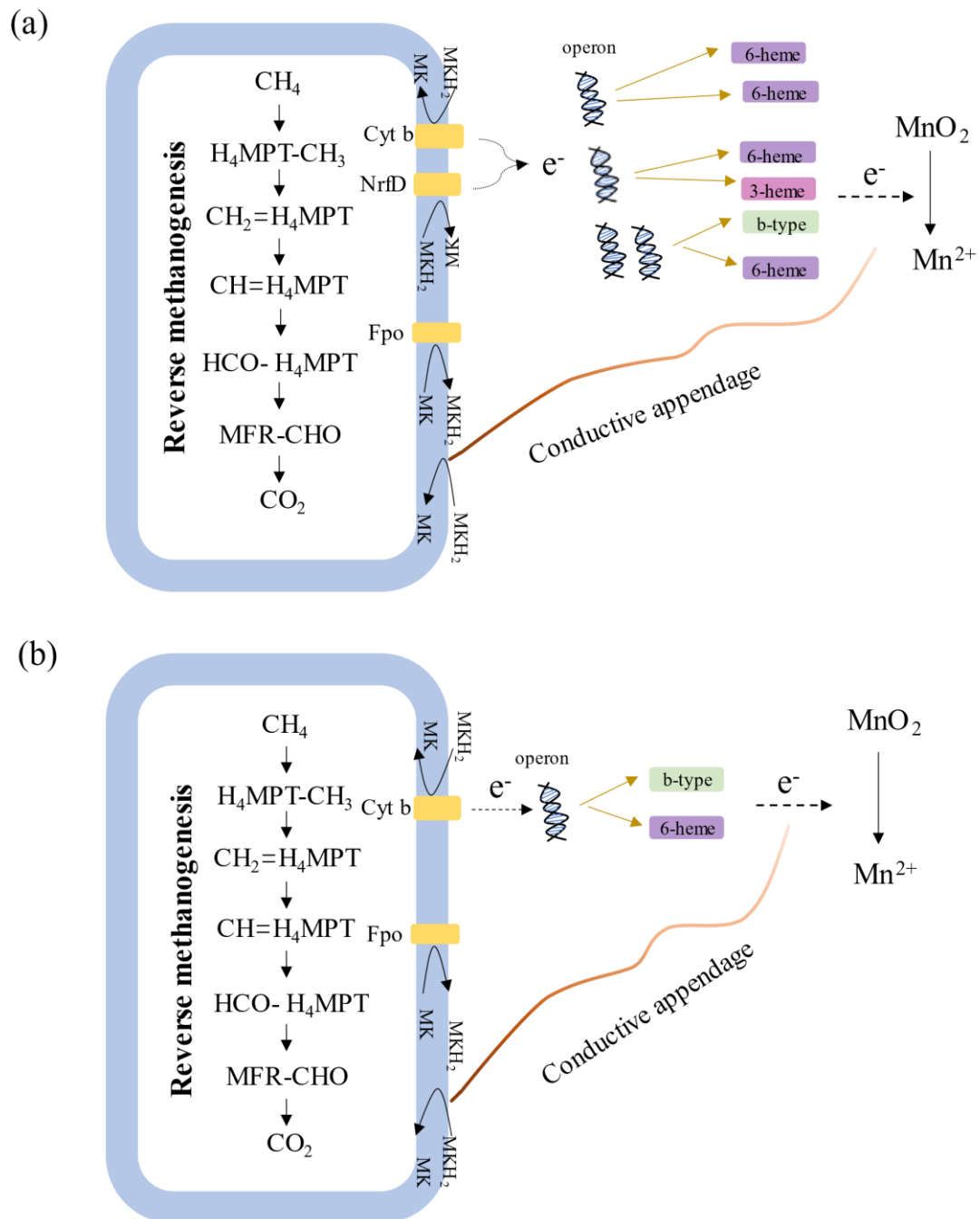Figure 3   Click here to access/download;Figure;Figure 3.docx ±

Figure 1 The Mechanisms of biological manganese oxide reduction coupled to methane oxidation coupled to (a) Ca. M. manganicus and (b) Ca.M. manganireducents
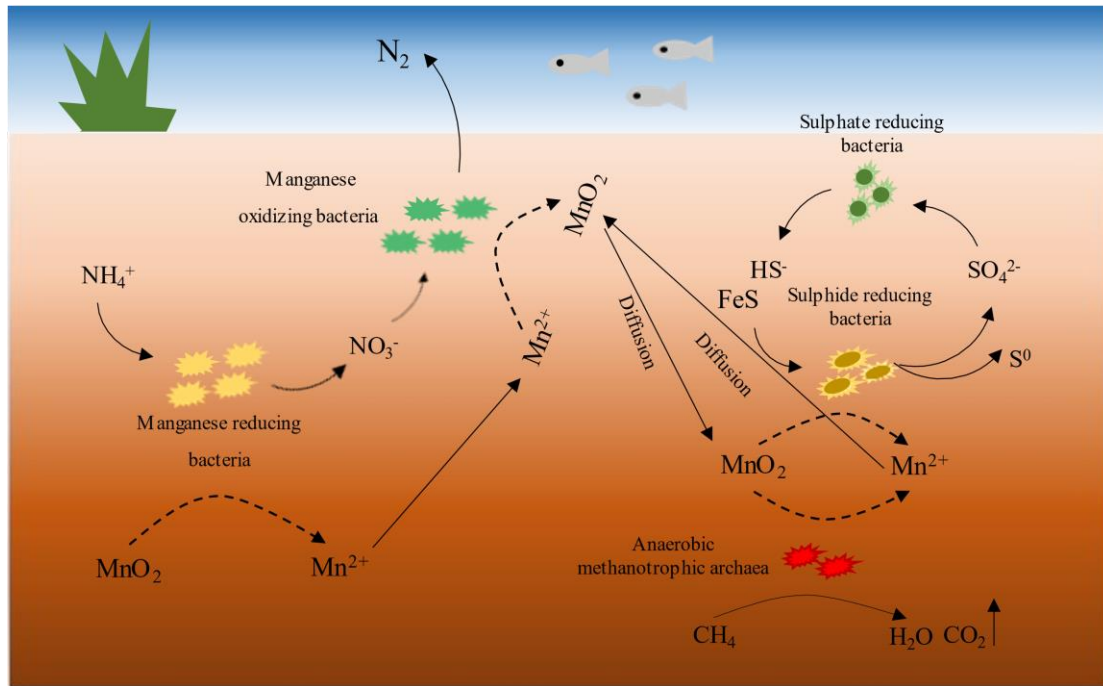
Figure 4

Figure 1 Possible N and S cycle coupled to biological manganese redox in the anaerobic environment