10. Summary

10.1. Introduction and context thesis

This thesis describes a research on the sedimentary cycling of iron and manganese in marine sediments. It extends the fundamental knowledge on the biogeochemical processes of sedimentary iron and manganese reduction. This knowledge, and the implementation in biogeochemical models, is necessary to explore utilisation of the processes for example in biological soil remediation, techniques to reduce methane emission from rice fields, and, still very speculative, as means to diminish the greenhouse effect by enhancing the oceans CO₂ fixation.

For the degradation of organic carbon, several microbial pathways exist. Different electron acceptors are used to oxidise the zero valent carbon in the organic matter to tetravalent organic carbon in carbon dioxide. In order of energy gain the processes are aerobic mineralization, nitrification, Mn-oxide - , Fe-oxide- and sulfate reduction and finally methanogenesis. The processes in which diffusive electron acceptors (O₂, NO₃, SO₄, and methanogenesis) are used are well studied.

Research on the pathways using the solid phase electron acceptors iron and manganese oxide has been intensified more recently, after the iron and manganese reducing bacteria were shown to be able to complete degradation of organic carbon. Under specific conditions, these metal oxide reduction processes are relatively important for the sedimentary organic carbon mineralization.

The field and experimental studies are performed with sediments originating from different environments covering a gradient of salinity and organic carbon input. A freshwater site, Appels, was situated along the Scheldt River in the intertidal zone and was flooded twice a day. The sediment was very fine and had a high organic carbon content due to high organic carbon input from benthic algae and particles from the Scheldt River and the adjacent marsh. Two subtidal estuarine sites in Lake Grevelingen were selected. One, Vliegertje, is a sandy littoral site situated on a plain, the other, Geul, is situated in a gully. Due to focussing of fine material the sediment in the gully was finer than the Vliegertje sediment. However, at both sites sediments were coarser than at the freshwater site Appels. Organic carbon inputs were much lower as well. A deep-sea sediment was sampled in the Eastern Mediterranean. These sediments are hemipelagic muds with a low organic carbon content and small grain sizes.
10.2. Iron oxide reactivity

In contrast to the diffusive electron acceptors, metal oxides exist in different forms. Amorphous oxides are relatively reactive and provide a high energy gain for bacteria when used for organic carbon mineralization, whereas crystalline oxides are less reactive, therefore energy gain is less when used as an electron acceptor. As energy gain is an important aspect, determining occurrence of a pathway, the composition of the sedimentary iron oxide pool is important information to estimate the potential for bacterial iron oxide reduction. Chemical iron oxide extractions using different types of leachants are used to determine the pool of iron oxides. However, these traditional iron oxide extractions only reveal large differences in the composition of the sedimentary iron oxide pool (mostly between sediments) whereas small changes (often within a profile) are not discerned. Besides, extraction results are affected by grain size and relative pool sizes and do not directly represent iron oxide reactivity. A kinetic method was used to describe the composition of the iron oxide pools in the three types of sediment. The method is based on a reactive continuum approach and results are independent of grain size and relative pool size. Results of the method used in the three types of sediments showed to be independent of pool distribution and grain size and the approach allows a quantification of iron oxide reactivity in sediments. Although a minimal pool of reactive iron oxides should be present in the sediment, the method reveals relatively small differences in iron oxide composition.

10.3. Limiting factors

The two components in microbial iron oxide reduction are iron oxide availability and degradable organic matter load. These two factors and their interaction determine sedimentary iron oxide reduction rates and the relative contribution of the iron oxide reduction process to organic carbon mineralization. Which factor is limiting for this process depends on sediment characteristics. Experiments showed that addition of organic carbon to aerobic Mediterranean samples moved the sediment to more favourable conditions for iron oxide reduction. Whereas conditions in the freshwater sediment were already favourable and addition of organic carbon moved the sediment to methanogenic processes besides addition of reactive iron oxides increased iron oxide reduction rates. In the estuarine sediment, the iron oxide reduction rates are determined by the minute balance between iron oxide availability and organic carbon concentrations. Maximal $V_{\text{max}}$ values can be reached as soon as sufficient degradable organic carbon is available. However,
realised iron reduction rates depend on the absolute concentration of reducible iron oxides.

10.4. Bioturbation

Bioturbation is an important process to preserve (sub) oxic sediment conditions and a relative important role for the sub-oxic organic carbon degradation processes such as metal oxide reduction. The effect of bioturbation on iron and manganese cycling depends on particle mixing and sediment irrigation. Experimental results show that both components are necessary to complete metal cycling and maintain the sub-oxic mineralization pathways using metal-oxides. Particle mixing, in the experiment mimicked by a mixing device, is important for (re) distribution of (re) oxidized metal-oxides. Irrigation, here imitated by enhanced sediment ventilation (i.e. enhanced exchange of porewater dissolved gases), is essential for the input of dissolved oxidants. However, the latter aspect is more important for manganese than for iron because iron has a higher affinity for oxygen and can also re-oxidise with manganese-oxides, while, because of the slow oxidation kinetics, a longer oxygen-Mn (II) contact is needed for sufficient retainment of Mn-oxide the sediment. Therefore, the efficiency of iron cycling is determined primarily by particle mixing. Whereas both particle mixing and irrigation determine manganese cycling efficiency. The experimental results indicate that the combined effect of ventilation and particle mixing on metal oxide cycling and reduction is not simply additive.

10.5. Field data

Determining organic carbon mineralization rates with the intermediate electron acceptors in sediments is complex because of interactions with other processes and constituents. Anaerobic bag incubations, to determine metal oxide reduction rates in different sediments, indicate that metal oxide reduction pathways may be important at intermediate to high organic carbon degradation rates. In organic poor Mediterranean sediments metal oxide reduction can be neglected as most of the mineralization occurred aerobically. However, slow metal oxide reduction will occur at greater depths. Intermediate organic carbon loaded estuarine sediments have higher rates of iron oxide reduction. In these sediments, both iron oxide reduction and sulfate reduction are important. In organic rich freshwater sediments, iron oxide reduction accounts for most organic carbon mineralization, with only a minor role for the other pathways like manganese reduction and
methanogenesis. These findings are consistent with model results and experimental data on factors limiting the importance of iron oxide reduction in mineralization.