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ANAEROBIC OXIDATION OF METHANE IN FRESHWATER ECOSYSTEMS

Anaerobic oxidation of methane (AOM) is a biochemical process that plays an important role in aquatic ecosystems, as it significantly reduces the emission of methane (CH_4) to the atmosphere. Under anaerobic conditions, CH_4 can be oxidized with electron acceptors, such as sulphates (SO_4^{2-}), nitrates (NO_3^-) or nitrites (NO_2^-), iron (Fe^{3+}), manganese (Mn^{4+}) and humic substances. The anaerobic oxidation of methane is mainly regulated by anaerobic methanotrophic archaea (ANME) and sulphate reducing bacteria. The AOM process is crucial to understand the CH_4 cycle and anticipate future emissions of the gas from water reservoirs. The process is widely described in marine environments, however very little is known about its occurrence and importance in freshwater systems. There is a great demand for this kind of the research, especially in ecosystems exposed to long-term anaerobic conditions, which may be in degraded reservoirs.

Keywords: anaerobic oxidation of methane, electron acceptors, methanotrophic archaea

1. Introduction

Methane (CH_4) is a gas emitted to the atmosphere from both natural and anthropogenic sources. It contributes to the greenhouse effect and global climate change [24]. Production of CH_4 occurs under anaerobic conditions with the participation of metanogenic archaea; in turn, methane oxidizing bacteria (metanotrophic archaea) contribute to reducing the emission of this gas to the atmosphere. Although aerobic methane-oxidizing bacteria (MOB) have been known for over 100 years [60], it was only at the turn of the last century that organisms involved in anaerobic oxidation of methane (AOM) were identified. Anaerobic methanotrophic archaea (ANME) are of great importance in regulating the Earth's climate, because they reduce the emission of large

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amounts of CH_4 accumulated in bottom sediments [32]. The process of anaerobic oxidation of methane (AOM) is widely described in marine environments, however very little is known about its occurrence and importance in freshwater systems [8; 26]. Just a decade ago, sulfates were the only known electron acceptor supporting anaerobic oxidation of methane [32; 38]; however, there are many other electron acceptors in the environment, such as: iron (Fe^{3+}), manganese (Mn^{4+}), nitrates (NO_3^-) [19] or nitrites (NO_2^-) [14; 48], which are thermodynamically more preferred than sulfates.

2. Anaerobic oxidation of methane

Methane emission from sediments is the net result of two processes: methanogenesis, which occurs in the hypoxic part of bottom sediments, and the oxidation of CH_4 as a result of aerobic or anaerobic microbiological processes [42]. AOM is an important process in marine and freshwater ecosystems [33; 44; 45], because it plays a key role in reducing the flow of CH_4 from bottom sediments to the overlying water, and thus also to the atmosphere [5; 34; 37]. AOM mainly occurs in the presence of methanotrophic archaea and sulfate-reducing bacteria [7]. AOM plays an important role in controlling CH_4 emissions in marine sediments, where it is oxidized on average 300–380 Tg $CH_4 \cdot yr^{-1}$ [20; 46]. It has also been estimated that, for example, in wetlands the AOM process can consume 4.1-6.1 Tg $CH_4/m^2 \cdot yr$, which is about 2-6% of the CH_4 emissions from wetlands in the world [23]. In the absence of oxygen, microorganisms can oxidize CH_4 in the presence of alternative electron acceptors, such as: sulfates, nitrates, nitrites, iron, manganese and humic substances [6; 7; 9; 14; 15; 18; 19; 21; 39; 45; 48; 49; 54; 56; 63].
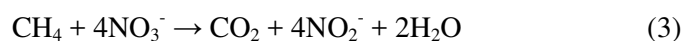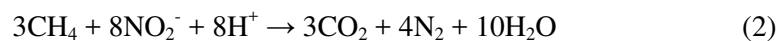
Anaerobic oxidation of methane coupled with sulfate reduction (AOM-SR) is the main process contributing to a significant reduction of methane produced in marine sediments. AOM-SR is regulated by a consortium of anaerobic methanotrophic archaea (ANME) and sulfate-reducing bacteria [32]. Methane is oxidized according to reaction:

$$CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O \qquad (1)$$
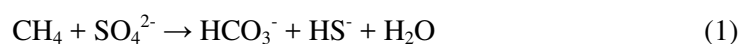
The AOM-SR process is influenced by the distribution of CH_4 and SO_4^{2-} in bottom sediments [26], as well as the stable isotopic composition $\delta^{13}C$-CH_4 [1]. There is little evidence of the role of this process in freshwater sediments, where the reduction of sulfate is limited. However, the results of the research presented in some publications [42; 51] indicate that AOM-SR can play a significant role in regulating the flow of CH_4 from sediments for SO_4^{2-} concentrations typical for freshwater reservoirs. AOM dependent from SO_4^{2-} concentrations have been demonstrated in the bottom sediments of Lake Cadagno (Switzerland) based on the isotopic analysis of carbon and archaea involved in the AOM. This process
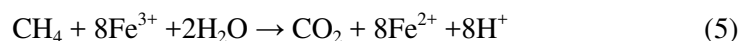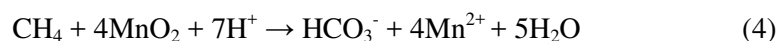
was particularly present near the surface of the sediment, where the concentration of SO_4^{2-} was > 2 mmol/l [52]. In turn, based on the research of some authors [42; 51], it was concluded that in a monomictic lake in Denmark (lake Ørn) high concentrations of sulfates may adversely affect the thermodynamics of the AOM process. Therefore, further research is needed to quantify the role of AOM in the CH_4 cycle in various freshwater environments.

Electron acceptors, i.e. nitrates, nitrites, iron and manganese, may play a potentially greater role in freshwater ecosystems [42]. Due to the fact that SO_4^{2-} concentrations are generally at low level in freshwater lakes, NO_3^- and NO_2^- may play a greater role in the AOM process. If nitrates and/or nitrites are available in anaerobic sediments, anaerobic bacteria oxidizing nitrates and/or nitrates take part in the AOM process. In this case, CH_4 can be used as an electron donor (reactions 2 and 3) [62], and sulfate reduction usually does not occur [50]. This process is called anaerobic oxidation of methane coupled with denitrification (AOM-D) [11; 41].

$$3CH_4 + 8NO_2^- + 8H^+ \rightarrow 3CO_2 + 4N_2 + 10H_2O \qquad (2)$$

$$CH_4 + 4NO_3^- \rightarrow CO_2 + 4NO_2^- + 2H_2O \qquad (3)$$

The AOM-D process is thermodynamically more favorable than AOM-SR. Therefore, AOM-D has become the subject of many scientific studies [14; 25; 45]. AOM-D was observed in lake sediments with a high concentration of NO_3^- [12; 37].

It is also possible to oxidize CH_4 by reducing manganese (Mn) or iron (Fe) (reactions 4 and 5) as confirmed by recent studies [6; 10; 53].

$$CH_4 + 4MnO_2 + 7H^+ \rightarrow HCO_3^- + 4Mn^{2+} + 5H_2O \qquad (4)$$

$$CH_4 + 8Fe^{3+} + 2H_2O \rightarrow CO_2 + 8Fe^{2+} + 8H^+ \qquad (5)$$

In the environment, iron reduction is often limited by the bioavailability of iron oxides, as iron (III) or complex iron compounds are not commonly found. In the publication of Ettwig et al. [17], the enrichment culture was incubated with more available metal forms: nanoparticle ferrihydrite (Fe^{3+}) and birnessite (Mn^{4+}). Selected electron acceptors supported the oxidation of CH_4 to CO_2, although the process itself was at a lower rate compared to nitrates and Fe (III) as iron citrate as electron acceptors. Stimulation of AOM after the addition of oxidized forms of Mn or Fe was observed in laboratory incubations of SO_4^{2-}– depleted freshwater sediments. It was found that iron reduction affects AOM in lake sediments, as indicated by higher $\delta^{13}C-CH_4$ values in deeper sediment layers [53]. AOM coupled with reduction of Mn and/or Fe was also observed in the water column of thermally stratified Lake Matano (Indonesia), the world's largest known ferruginous reservoir [10]. These studies have shown that the role

of Mn and Fe oxides in AOM is indirect and involves the stimulation of oxidative sulfur circulation, which can supply SO_4^{2-} to AOM-SR. Based on the study of lake Ørn sediments (Denmark), it was concluded that the process took place at significant depths, where both iron and sulfates were present in low concentrations, confirming the significance of AOM-Fe/Mn in Fe/Mn–depleted sediments. Furthermore, anaerobic reduction of iron (Fe^{+3}) and manganese (Mn^{+4}) coupled with AOM is regarded as more favorable process; and it has been shown that it is a significant process in lakes [42; 53]. Little is known about the microorganisms involved in AOM-Fe/Mn. However, on the basis of the conducted research [6], it was noticed that a large group of microorganisms of AOM-Fe/Mn in sediments after incubation were microorganisms associated with the marine benthic Archaea group D and ANME [42].

The rate of anaerobic oxidation of CH_4 depends not only on the availability and concentration of anaerobic oxidants, but also on the weather conditions and physical factors prevailing on the reservoir, such as water turbulence [3; 31]. High wind speeds can lead to complete mixing of the reservoir waters in a short time, e.g. in autumn . Therefore, the majority of CH_4 can be emitted to the atmosphere due to increased transport through different water layers and a short residence time in the water column [3; 29]; on the other hand, gradual mixing of reservoir water may cause that CH_4 will be longer available for bacteria participating in AOM [29], which will reduce its emission to the atmosphere.

3. Anaerobic methanotrophic archaea

Anaerobic methanotrophic archaea (ANME) are involved in anaerobic methane oxidation – in the process opposite to methanogenesis [32]. Based on the phylogenetic analysis of the 16S rRNA gene, ANME were divided into three groups: ANME-1, ANME-2 and ANME-3 [8; 21; 33; 40]. All ANMEs are phylogenetically linked to various groups of methanogenic archaea. ANME-2 and ANME-3 belong to the order *Methanosarcinales*; in turn, ANME-1 belong to the order related to *Methanosarcinales* and *Methanomicrobiales* [32]. ANME-3 are closely related to the *Methanococcoides* gene. Microorganisms belonging to the ANME-2 and ANME-3 groups have a shape similar to methanogens of *Methanosarcina* and *Methanococcus*; whereas ANME-1 show a different morphology. ANME strains occur in anaerobic freshwater sediments, as well as in marine environments, aquifers and soils [32; 58].

AOM-SR is a metabolic process combined with SO_4^{2-} reduction, obtaining energy through syntrophic consortium of the ANME and sulfate reducing bacteria (SRB) [7; 22]. Some SRB groups: *Desulfosarcina*/*Desulfococcus* and *Desulfobulbaceae* participate in the sulfate reduction (SR) process together with ANME. However, it has been shown that some ANME filotypes perform SR without the presence of SRB in various aquatic environments [2; 35; 36; 59; 61], suggesting that AOM-SR may occur regardless of the occurrence of ANME [38].

In addition, Ettwig et al. [14] showed that AOM can be mediated via *Candidatus Methylomirabilis oxyfera* (NC10 type) in the presence of NO_2^-. The bacterium can produce oxygen by reducing NO_2^- and use the O_2 to oxidize CH_4 [11; 14]. *Methylomirabilis oxyfera*, an NC10 bacterium, and *Candidatus Methanoperedens nitroreducens*, ANME archaea, have been identified as microorganisms capable of carrying out AOM-D [14; 19; 37]. Denitrification metanotrophs seem to be common in freshwater sediments, as determined by 16S rDNA studies [16], but the quantitative role of NO_3^- or NO_2^- in AOM under natural conditions has not been studied so far.

AOM associated with the reduction of soluble iron complexes have recently been observed in environments rich in ANME-2 [49], and AOM coupled with reduction of iron or manganese oxides has been confirmed several times and presented in many scientific publications [6; 13; 43; 47; 53]. In addition to the ability of these bacteria to carry out AOM along with iron reduction in enrichment cultures [17], it was found that ANME-2d or AAA (*AOM-associated archaea*) containing *Candidatus Methanoperedens nitroreducens* carry out AOM-SR in the sediments of the alpine lake Cadagno (Switzerland) [52; 57]. Recent studies have concluded that the strain closely related to *Candidatus Methanoperedens nitroreducens* from freshwater enrichment culture is present during AOM coupled with the reduction of soluble and nanoparticulate iron forms [17].

Methane oxidizing bacteria not only reduce atmospheric CH_4 emissions, but also provide adequate nutrients for aquatic consumers [27]. In several scientific publications [4; 28; 30; 55] the role of CH_4 oxidizing bacteria was examined as a carbon source for zooplankton in humic lakes with thermal stratification of water. Kankaala et al. [30] showed that metanotrophs were a source of nutrients for a typical pelagic zooplankton – Daphnia. The authors also suggested that carbon from CH_4 plays a greater role in the trophic network of lakes than it was previously estimated.

4. Summary

Freshwater ecosystems are identified as one of the main natural sources of methane, but little is known about the importance of anaerobic methane oxidation (AOM) in these ecosystems. The emerging publications of many authors show that AOM can significantly reduce methane emissions from freshwater sediments. The study of the activity of microorganisms taking part in AOM and the ongoing metabolic processes with the participation of electron acceptors (Fe^{3+}, Mn^{4+}, SO_4^{2-}, NO_3^-, NO_2^-) is crucial in understanding the circulation and predicting future CH_4 emissions. The flow of methane into the atmosphere from aquatic ecosystems is regulated by two main groups of microorganisms. Methanogenic archaea are responsible for the production of CH_4, while methane-oxidizing bacteria (ANME) are responsible for the

consumption of CH_4 in these ecosystems. Different electron acceptors contained in sediments affect the presence of various groups and species of microorganisms characteristic of individual processes: AOM-SR, AOM-D and AOM-Fe/Mn. In marine environments, the dominant process is AOM coupled with sulfate reduction. In freshwater ecosystems, this process is probably limited by low sulfate concentrations. The methane oxidation processes associated with the reduction of alternative electron acceptors such as: nitrates/nitrites, manganese and iron are more significant there.

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