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Changes of methanogenic pathways in freshwater sediments – an incubation experiment

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Introduction

Methane is one of the latest products of microbial decomposition of organic matter. It is produced in marine or freshwater anaerobic sediments mainly due to acetate fermentation or CO_2 reduction pathway. In recent studies the carbon isotope analysis are commonly used to distinguish methanogenic pathways and to establish sources of methane. The $\delta^{13}C$ value is also considered in mass balance calculation of methane in the atmosphere. Such calculation is difficult because carbon isotope composition of methane undergoes spatial and temporal variations (e.g. Jędrysek 1995, Hornibrook 2000). The reason of $\delta^{13}C(CH_4)$ variations in particular environments is still enigmatic, but four main factors are considered to be responsible of that: 1) changes of methanogenic pathways, 2) availability of substrates, 3) temperature variations and 4) spatial distribution of labile organic carbon in depth profiles of sediments or water reservoirs.

In this paper we consider the changes of methanogenic pathways relative to the availability of labile organic carbon and time of decomposition of organic matter in freshwater sediments. Miyajima et al. (1997) has evidenced that increased recalcitrance of soil organic matter results in greater production of CH_4 through the CO_2 reduction pathway in tropical wetlands. The same conclusion was done by Hornibrook et al. (2000) in freshwater wetlands, who suggest that the lower rate of methanogenesis based on acetate fermentation is a result of decrease of labile organic carbon with increasing recalcitrance of biodegraded organic matter. To test this thesis we incubated freshwater sediment under long time interval (570 days). The studied incubator is near closed system, because the sediment with organic matter was put in it once. Only gases produced in the sediment would undergo the exchange with atmosphere during the incubation and sampling. The accept procedure of incubation allowed tracing changes in substrate availability for methanogenesis due to increase of recalcitrance of organic matter enclosed in the incubated sediment.

Methods and results

The data presented come from one incubator. The incubation method and the source of incubated sediment were described by Szynkiewicz et al. (this volume). During 570 days of incubation, in one month intervals, the concentrations and $\delta^{13}C$ values have been analyzed in:

- methane in pore gases in the sediment,
- organic matter in the sediment
- DIC in the sediment/water interface.

After each sampling action, the sediment was mixed with water column to remove the CH_4, which still left in the sediment as well as to homogenize DIC concentration and $\delta^{13}C$(DIC) in the water column and sediment.

In the course of 570 days of the incubation, the permanent decrease of CH_4 concentration (from 86 to 39 %) and increase of $\delta^{13}C(CH_4)$ values (from –68.90 to –61.37 ‰) in the incubated sediment have been observed (Fig. 1). However, the concentration of organic matter in the sediment varied independently from 1.02 to 2.03 % (Fig. 2). The $\delta^{13}C$ value of organic matter showed very narrow range from –28.10 to –27.54 ‰. The concentration of DIC in the sediment/water interface showed weak decreasing trend (R = -0.47; Fig. 3) and varied widely along the incubation time from 100.68 to 216.62 mg/l. However, the $\delta^{13}C$(DIC) value showed permanent decreasing trend (R = -0.85; Fig. 3) from –6.33 to –12.04 ‰.

Discussion

Methane originated from acetate fermentation shows higher values of $\delta^{13}C$ (from –65 to –50 ‰) as compare to the methane from CO_2 reduction (from –110 to –60 ‰). The acetate is a fermentative product of easy degradable organic compounds and represents fraction of labile organic carbon in sediments. It is also well documented that acetate is probably the main substrate for methanogenesis in freshwater sediments. In our opinion, during the incubation, the acetate fermentation was the main methanogenic pathway. The obtained $\delta^{13}C(CH_4)$ values were typical for this process. We did not measure the acetate concentration and $\delta^{13}C$ value of the acetate, but the observed increase of $\delta^{13}C(CH_4)$ and decrease of methane concentration (Fig. 1) may be resulted from depletion of acetate in the incubated sediment.

There is no evidence of methanogenesis due to CO_2 reduction. Moreover, increasing recalcitrance of organic matter with time of incubation did not cause the change of methanogenic pathway toward CO_2 reduction, like we expected. This pathway involves higher carbon isotope fractionation and $\delta^{13}C(CH_4)$ values are distinctively lower than these from acetate fermentation. The $\delta^{13}C(DIC)$ values at the sediment/water interface became more negative along the incubation (Fig. 3). For that reason we are convinced that changing of methanogenesis toward CO_2 reduction would reflect in lower $\delta^{13}C$ value of methane at the end of the experiment. However, the obtained data evidenced that methanogenesis was probably dependent mainly on the acetate pool in the incubated sediment, which became enriched in ^{13}C along the entire incubation. In spite of this, it is not clear why the concentration of total organic matter showed higher variations and did not decrease along the incubation (Fig. 2). We suspect, that probably some microbial processes, especially in water column, could influence the supply of fresh organic matter. On the other hand, it is enigmatic why these processes did not influence the amount of acetate in the incubated sediment.

The presented data suggest, that activation of methanogenesis due to CO_2 reduction probably requires higher concentration of DIC (CO_2 or HCO_3^- ion) in the sediment. It is usually considered, that limiting factor of this pathway is H_2 production in the sediments. However, it could rather influence for methane concentration in the pore gases of sediment along the entire incubation. Even though, $\delta^{13}C(CH_4)$ should express more negative values relative to decreasing trend of $\delta^{13}C(DIC)$ values along the incubation.

The important role of DIC concentration in the process of methanogenesis due to CO_2 reduction was also confirmed by the incubation of the same sediment under elevated concentration of SO_4^{2-}. The intensive oxidation of acetate by sulphate reducers in this incubator involved higher production of CO_2, what activated methanogenesis due to CO_2 reduction (Szynkiewicz et al. – see this volume) and the availability of H_2 was not the limiting factor in this case.

The CO_2 reduction pathway is commonly observed in deeper profiles of sediments. They are generally characterized by higher concentration of pore gasses collected in various stages of microbial decomposition of organic matter. In our experiment the concentration of DIC was always diluted after each sampling due to mixing the water with sediment. Probably, this procedure limited DIC concentration, thus also the CO_2 reduction. For that

reason methanogenesis was mainly dependent on the availability of acetate in the incubated sediment.

Conclusion

1. The acetate fermentation was the main methanogenic pathway in the incubated sediment.
2. Increasing recalcitrance of organic matter along the time of incubation did not cause the change of methanogenic pathway toward CO_2 reduction.
3. Probably, higher concentration of DIC is required to activate the CO_2 reduction pathway. Such conditions are common in deeper profiles of sediments, where the produced gases are stored for a longer time.

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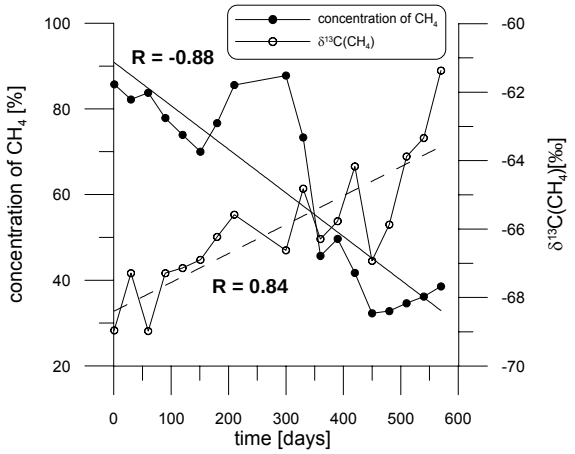

Fig. 1. Variations of methane concentration and their $\delta^{13}C$ value along the 570 days incubation.

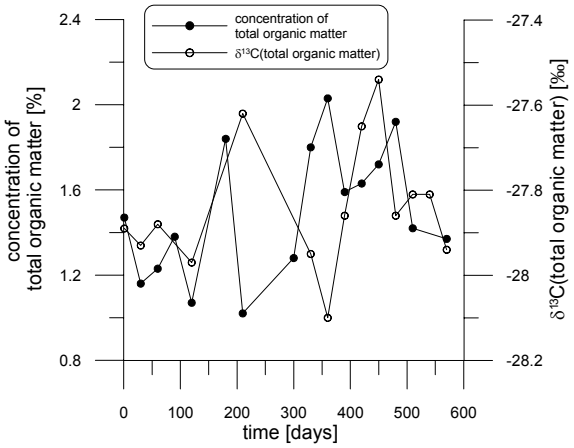

Fig. 2. Variations of total organic matter concentration and their $\delta^{13}C$ value along the 570 days incubation.

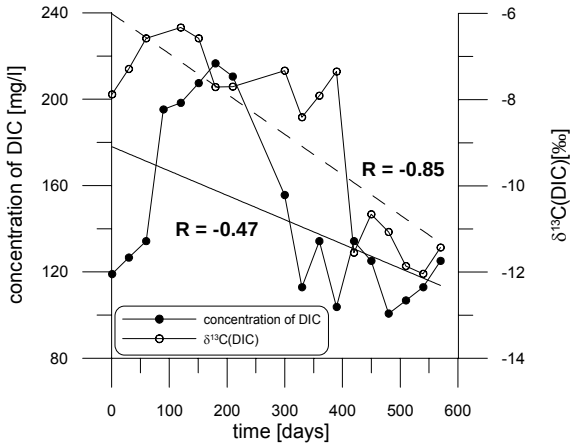

Fig. 3. Variations of DIC concentration and their $\delta^{13}C$ value in the sediment/water interface along the 570 days incubation.