CATALYTIC EFFECT OF VARIOUS METAL IONS ON THE METHYLATION OF MERCURY IN THE PRESENCE OF HUMIC SUBSTANCES

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Abstract. Methylation of Hg$^{2+}$ ($\text{Hg(NO}_3\text{)}_2$) in the presence of fulvic acid (FA) and various metal ions has been studied. The concentrations of Hg$^{2+}$ and FA ranged from 5 to 20 mg L$^{-1}$ and 171 to 285 mg L$^{-1}$ DOC, respectively. The pH range was 3 to 6.5. FA was isolated from an acid brown-water lake by XAD-8 polymeric adsorbent. Methylmercury production in the dark during 2 to 4 days incubation at 30 °C increased with increasing concentrations of Hg$^{2+}$ ion and FA as well as with additions of metal ions ($5 \times 10^{-5}$ mole L$^{-1}$). The observed catalytic activity of metal ions followed the order Fe$^{3+}$ (Fe$^{2+}$) > Cu$^{2+}$ > Mn$^{2+}$ > Al$^{3+}$. The production of methylmercury had a pH-optimum around 4 to 4.5 at the conditions tested.

1. Introduction

The microbial methylation of Hg in sediments (Jensen and Jernelöv, 1967, 1969) has been regarded, since its discovery, as the dominant source for the accumulation of methylmercury in fish. Biological methylation and demethylation of Hg have been studied by many scientists using various experimental conditions and microbial isolates (Wood et al., 1968, 1972; Landner, 1971; Bisogni and Lawrence, 1975; Furukava et al., 1969). It was found that also several chemical substances containing active methyl-donors may methylate inorganic Hg under suitable conditions (Wood, 1972; Akagi et al., 1972; Kitamura and Sumino, 1972). The recently found abiological methylation in the presence of humic substances reported by Rogers (1976, 1977) and Nagase (1982) may be a generally occurring methylation process and thus of importance for the present methylmercury loading in the biota. They both found that the low molecular weight compounds of a humus fraction (fulvic acids) were the more active compounds in the methylation. This formation of methylmercury was also pH-dependent with optimum conditions around pH 4.

In this paper some laboratory experiments are reported which show that the methylation rate of Hg by humic substances may also be dependent upon the presence of some metal ions. Relatively low concentrations of both Hg$^{2+}$ and fulvic acid comparing with others (Nagase, 1982; Rogers, 1977), have been used in this investigation. To be able to evaluate the possible environmental significance of this specific methylation process and factors that influence the process, further investigations are planned to cover more extensively the physico-chemical parameters and to study the mechanisms.
2. Experimental

2.1. Isolation of Fulvic Acid

One hundred seventy liters of lake water (pH = 5.7, color = 130 mg Pt L\(^{-1}\)) were taken from a lake with high methylmercury concentration in fish (concentration in Northern Pike, *Esox lucius*, 1–2 mg kg\(^{-1}\) muscle). Fulvic acid (FA) was isolated from the water sample by using Amberlite XAD-8 polymeric adsorbent (Thurman and Malcolm, 1981). The sample was filtered through glass wool and then adjusted to pH less than 2 before it was passed through a XAD-8 column. The FA and humic acid (HA) were eluted with 0.1 N NaOH. The alkaline eluate from the XAD-8 resin was acidified to pH < 2 using concentrated HCl, and recycled through the XAD-8 column. The eluate was finally passed through a cation exchange resin to remove all sodium ions and other metal ions. The FA solution was separated from the HA precipitate by acidification of the concentrated eluate. The obtained stock solution of FA which was 10 to 17 times higher in concentration than the solution used in the following experiments was analyzed with respect to relevant elements. The result is shown in Table I. The FA’s used in the presented investigation were not sterilized.

<table>
<thead>
<tr>
<th>org. C</th>
<th>N</th>
<th>Al</th>
<th>Cu</th>
<th>Fe</th>
<th>Mn</th>
<th>Pb</th>
<th>KMnO(_4) value</th>
</tr>
</thead>
<tbody>
<tr>
<td>2860</td>
<td>41.6</td>
<td>2.29</td>
<td>0.884</td>
<td>2.60</td>
<td>0.216</td>
<td>0.0754</td>
<td>17160</td>
</tr>
</tbody>
</table>

* The concentration of Hg was 0.004 mg L\(^{-1}\).

2.2. Experimental Method

The reaction of inorganic Hg with FA was studied at 30 °C by incubating 50 mL solution containing FA, mercuric nitrate, chloride (\(\approx 10^{-4}\) mole L\(^{-1}\)) and other metal ions for 2 to 4 days in the dark. The concentration of Hg\(^{2+}\) varied from 5 to 20 mg L\(^{-1}\) FA from 171 to 285 mg L\(^{-1}\) organic C and pH from 3 to 6.5. The metal ions tested were Fe\(^{2+}\), Fe\(^{3+}\), Cu\(^{2+}\), Mn\(^{2+}\), and Al\(^{3+}\) and their concentrations ranged from 5 to 10 \(\times 10^{-5}\) mole L\(^{-1}\). They were added with the intention to study their possible catalytic effect on the methylmercury (CH\(_3\)Hg\(^{+}\)) formation.

After incubation, the methylmercury produced was analyzed by a modified extraction method based on Westöö’s method (1966) (See Figure I) and a gas chromatograph method using an electron capture detector. The precision of the total analysis of methylmercury was about ± 0.5 ng as Hg in the 50 mL sample.

In order to evaluate the efficiency of the extraction procedure for CH\(_3\)Hg\(^{+}\), several standard solutions (50 mL) containing 5 to 140 ng CH\(_3\)HgCl as Hg were examined. The extraction undertaken resulted in 67\% (± 4\%) recovery of the CH\(_3\)HgCl initially