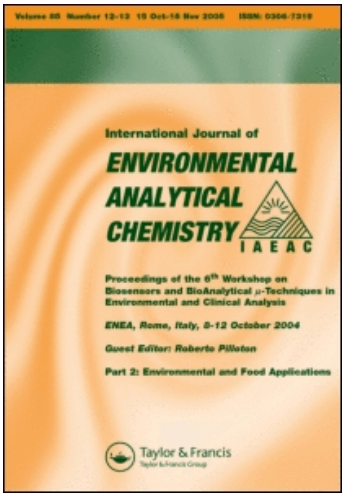


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# Determination of Concentration Profiles of Methyl Mercury Compounds in Surface Waters of Polar and other Remote Oceans by GC-AFD

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# DETERMINATION OF CONCENTRATION PROFILES OF METHYL MERCURY COMPOUNDS IN SURFACE WATERS OF POLAR AND OTHER REMOTE OCEANS BY GC-AFD

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The concentration of monomethyl mercury ($MeHg^+$) and dimethyl mercury ($Me_2Hg$) was determined in surface sea-water samples of the Antarctic and Arctic Ocean as well as of other remote areas (South Atlantic and South Pacific) during expeditions of the German research vessel "Polarstern". A purge and trap/gas chromatographic system, equipped with an atomic fluorescence detector (AFD), was used. For the analysis of $MeHg^+$ conversion into the volatile methylethyl mercury by reaction with tetraethyloborate prior to the purging process was carried out. The detection limit for both methylated mercury compounds was 5 pg Hg/L, which allowed their determination in most ocean water samples even in those of the Antarctic and Arctic Ocean. A north-south concentration profile in the Atlantic Ocean, covering a distance from 51°N to 58°S, was also examined, which resulted in the most extended set of data in the environment for these important heavy metal species. In anthropogenically influenced areas of the North Atlantic from 51°N to about 40°N concentrations of methylated mercury in the range of 100-3000 pg/L were found. The contents of these species were significantly lower in remote areas, represented by a range of <5 pg/L to 150 pg/L. Concentrations of the methylated mercury species were compared with those of substances often used as biomass indicators, e.g. chlorophyll-a and adenosine triphosphate. A positive correlation was found, in general, in remote areas between the contents of methylated mercury and these parameters for bioactivity, demonstrating the biogenic origin of $MeHg^+$and $Me_2Hg$, respectively. The concentration of $MeHg^+$ normally exceeded that of $Me_2Hg$, except at locations with especially high bioactivities. This result indicates that $Me_2Hg$ may be the main primary biogenic product. Oceanographic conditions are very well reflected by concentration profiles of methylated mercury. For example, in biologically very active upwelling regions peak concentrations of $Me_2Hg$ and $MeHg^+$ were found, whereas in parts of the Antarctic Ocean, totally covered by ice, the concentration of methylated mercury was determined to be below the detection limit.

*Keywords:* Monomethyl mercury; dimethyl mercury; concentration profiles in surface ocean water; Antarctic and Arctic Ocean; Atlantic; GC separation; atomic fluorescence detection

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## INTRODUCTION

The different processes, which influence the global biogeochemical cycle of mercury have not been clearly identified until today. Depletion of mercury in surface ocean water was observed in areas of enhanced biological activity, apparently due to the transfer of a volatile mercury compound from the ocean's surface into the atmosphere.[1] An enrichment of mercury in the marine atmosphere is an important consequence of this transfer mechanism.[2–4] Biogenic production of volatile organomercury compounds such as $Me_2Hg$ is therefore an integral part of the cycle of mercury in the environment. In other oceanic areas, especially in those where the atmosphere is affected by anthropogenic substances, a net uptake of atmospheric mercury by deposition on the sea-water surface is possible.

There is a lack of analytical data for organomercury species in sea-water. Only a few attempts have been made, up to now, to measure such mercury species in sea-water. Determinations near the shore found monomethyl mercury at a concentration level of about 2 ng/L.[5,6] Fitzgerald et al. carried out measurements in the open Pacific Ocean, where the concentration of the methyl mercury compounds was found to be much lower (pg/L range).[7–10]

Because high biological activities are found in the Antarctic and Arctic Ocean, biomethylation of mercury, unaffected by anthropogenic influences, can be expected in these polar waters. Therefore, the main objective of this work was the application of a sensitive method (gas chromatographic separation coupled with atomic fluorescence detection) for the determination of methyl mercury compounds in the Antarctic and Arctic Ocean as well as of their north-south distribution.



## EXPERIMENTAL

### Chemicals

Monomethyl and dimethyl mercury, for preparation of standard solutions, and sodium tetraethyloborate $NaBEt_4$ were obtained from Alfa Ventron, sodium acetate and acetic acid from Merck. A solution of $NaBEt_4$ (1 % by weight) was freshly prepared with bidistilled water every 3 to 4 days and stored at 4°C in the dark. For the sodium acetate buffer, sodium acetate (27 g) and acetic acid (12 mL) were dissolved in bidistilled water to result in a final volume of 100 mL.

## Sampling

The sea-water samples were taken during different expedition legs of the German research vessel "Polarstern": ANT XI/1 (October/November 1993; from Bremerhaven, Germany, southwards along the Atlantic Ocean to the pack-ice border at about 58°S, then northwards to Capetown), ANT XI/2 (December 1993/January 1994; from Capetown in an easterly/south-easterly direction to Punta Arenas, Chile), ANT XII/4 (end of March until middle of May 1995; from Punta Arenas along the Pacific part of the Antarctic Ocean to Rothera on the Antarctic Peninsula at 68°S and back to Punta Arenas), and ARK X/1 (beginning of July to middle of August 1994; from Bremerhaven northwards into the Greenland Sea at about 79°N, then south-easterly to Tromsø, Norway). The samples were obtained from a snorkel system, which continuously pumped sea-water under clean conditions from the front of the ships bow at a depth of 10 m into the laboratory, where the samples were filled into precleaned PE bottles.



## Derivatization and preconcentration

After being filtered, using an 0.45 μm pore sized filter, 100 mL of the sample were injected with a syringe into the purging unit of the purge & trap GC-AFD system (Figure 1). Dimethyl mercury could directly be purged, whereas monomethyl mercury must be converted into a volatile compound, which was carried out by derivatization analogous to literature descriptions.[11] This derivatization involved in situ ethylation of $MeHg^+$ by sodium tetraethyloborate in a buffered aqueous solution. 200 μL of the acetate buffer solution were added to the sample adapting the pH value to five. 50 μL of the sodium tetraethyloborate solution were then added and the mixture was allowed to react without purging for 10 min. This in situ ethylation quantitatively formed methylethyl mercury (MeEtHg) from $MeHg^+$ but has no effect on the original dimethyl mercury in the sample. Inorganic mercury ions $Hg^{2+}$, which were also present in the ocean water samples, were only partially converted into diethyl mercury ($Et_2Hg$). This derivatization method is therefore not useful for determinations of $Hg^{2+}$ ions.

The sample was then degassed with helium at a flow rate of 200 mL/min for 60 min until all volatile substances were completely purged. The purging unit was equipped with a sintered glass plug to produce small helium gas bubbles and, thereby, to increase the efficiency of the purging procedure. The volatile substances were transferred with the carrier gas into the cold trap, which was cooled with liquid nitrogen. A drying tube, filled with dried and precleaned potassium carbonate, was installed between the purging unit and the cold trap to

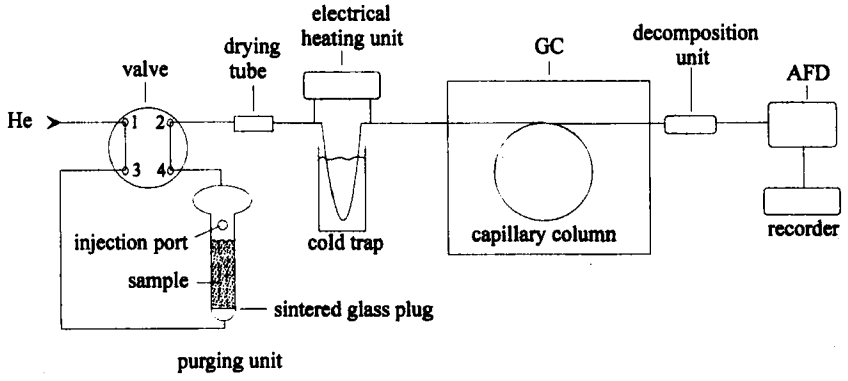


FIGURE 1 Schematic figure of the purge and trap system coupled with GC/AFD for the determination of volatile organomercury compounds in marine water samples (valve position 1–3, 2–4 for purging of samples; 1–2, 3–4 for analysis of samples)



prevent clogging of the cold trap by moisture. During the purging process the valve was switched in the 1–3, 2–4 position (Figure 1).

## Gas chromatography

After completing the purging process, the valve was switched into the injecting position 1–2, 3–4 (Figure 1). The trapped substances were transferred into the capillary column of the GC by removing the liquid nitrogen and by direct heating of the cold trap using an electrical heating unit. This procedure ensured a fast and complete transport of all trapped substances into the gas chromatographic system. For separation of the different compounds a capillary column (DB 5, length 10 m, film thickness 0.50 μm, inner diameter 0.53 mm) was applied in the gas chromatograph, type Sigma 3 (Perkin Elmer). The temperature program was as follows: 2 min at 40 °C, heating up with a rate of 20 °C/min to 100 °C, 5 min at 100 °C. These conditions resulted in sharp peaks and secured baseline separation of the investigated substances (Figure 2). Subsequent detection with an atomic fluorescence detector (AFD), type CVAFS 2 (Brooks Rand), was performed after decomposition of the organomercury compounds at about 830 °C to elementary mercury. The sensitive detection of organomercury compounds by atomic fluorescence spectrometry after decomposition was already used successfully in the past.[9,12] A representative chromatogram of one of the ocean water samples is shown in Figure 2. As can be seen, the three volatile species dimethyl mercury, methylethyl mercury and diethyl mercury are clearly separated and appear at

retention times of 1.5 min, 3.6 min and 5.1 min, respectively. The detection limit obtained was 5 pg Hg/L for both compounds, $MeHg^+$ and $Me_2Hg$. The calibration curve was found to be linear over the whole concentration range to be determined, from the detection limit up to 3 ng/L (correlation factor of 0.998).

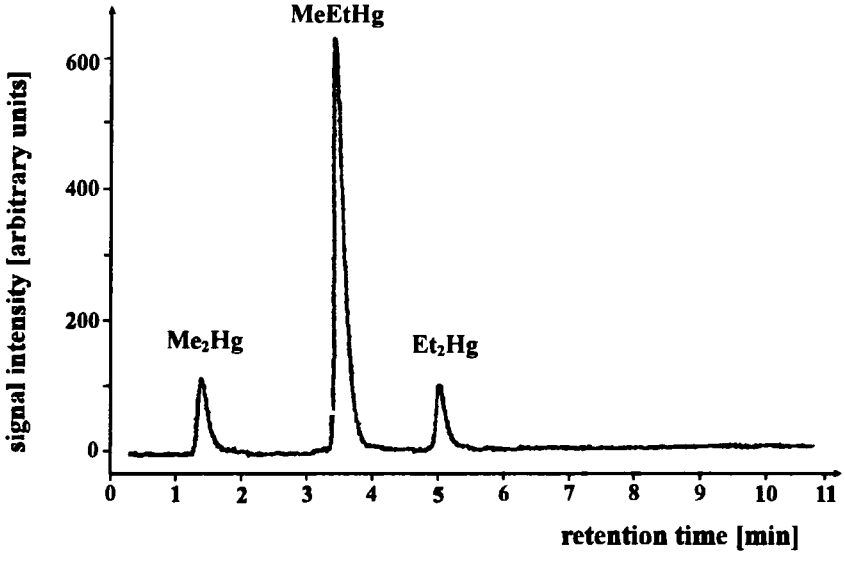


FIGURE 2 GC/AFD chromatogram of the volatile organomercury compounds dimethyl mercury ($Me_2Hg$), methylethyl mercury (MeEtHg) and diethyl mercury ($Et_2Hg$)



## RESULTS AND DISCUSSION

### North-south profile of methyl mercury compounds (expedition ANT XI/1)

A north-south profile of the concentration of the methyl mercury species $MeHg^+$and $Me_2Hg$ from 51°N to 58°S is represented in Figure 3, a more detailed picture of data south of 30°N is given in the lower diagram of Figure 4, where the concentration scale is extended by a factor of about 20. Monomethyl mercury and dimethyl mercury could be detected in most of the ocean water samples. The contents of both species are especially high at latitudes from 51°N to about 40°N, with peak concentrations of about 3000 pg/L at the beginning of the cruise. South of 30°N concentrations vary between the detection limit of 5 pg/L and about 150 pg/L. An indication for the reason of these differences between the anthropogenically influenced nothern part of the Atlantic Ocean and the more or less remote southern part was obtained by concentration depth profiles in these

different areas (Figure 5). In the case of the anthropogenically influenced area, the $MeHg^+$ and $Me_2Hg$ concentrations continuously decrease from the water surface to a depth of about 100 m. Then, concentrations nearly remain constant at a low level. In contrast to that concentrations for the depth profile of samples from the remote area are low at the surface down to about 40 m but they show a significant maximum at about 60 m. This concentration peak between about 40 m and 100 m is at the same depth where normally the main bioactivity occurs in the ocean, which was confirmed for this special depth profile by the chlorophyll-a content.[13] These results clearly indicate biogenic production of $MeHg^+$ and $Me_2Hg$. Whether the different concentration profile of the anthropogenically influenced region is only an effect of the higher mercury input into the surface layers of the ocean from the atmosphere or a result of increased bioactivities in the upper layers by contaminations, must be investigated in more detail in the future. However, Pongratz and Heumann have shown in model experiments that polar macroalgae increase their production rate for $MeHg^+$and $Me_2Hg$ by a factor of 2-10 when the total natural mercury content in ocean water (about 0.8 ng/L) is doubled by the addition of inorganic $Hg^{2+}$.[14]



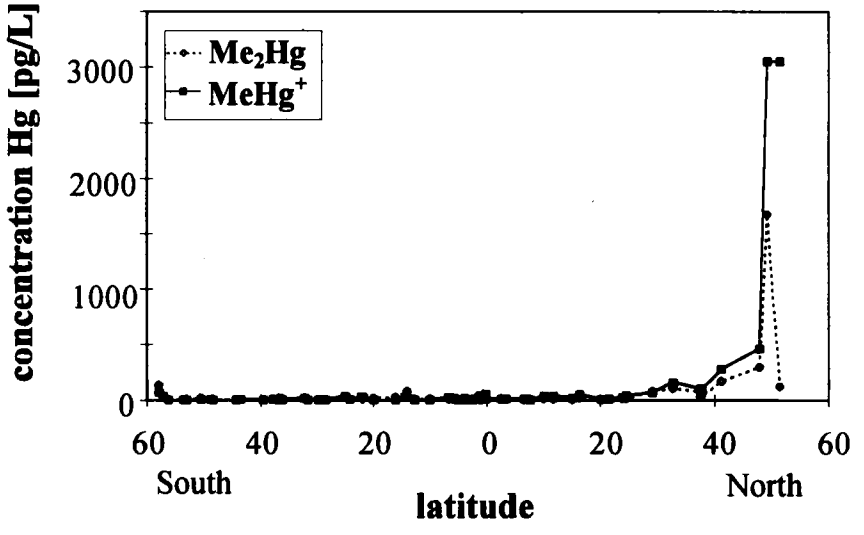


FIGURE 3 North-south concentration profile of $MeHg^+$ and $Me_2Hg$ in surface sea-water samples of the Atlantic Ocean from 51°N (British Channel) to 58°S (pack-ice border of Antarctica)

Besides the contents of methyl mercury compounds, Figure 4 also represents the concentration of ATP (adenosine triphosphate) and TTI (tritiated thymidine incorporation) in surface water samples of the Atlantic Ocean from 30°N to

58°S, which were determined by other groups.[15,16] ATP is used as an universal biomass parameter, whereas TTI is an indicator for bacterial activities. It is of special interest that the highest ATP and TTI values correlate with a maximum in the $Me_2Hg$ concentration at 15°S. Whereas in most of the surface water samples the content of monomethyl mercury exceeds that of dimethyl mercury, the $Me_2Hg$ concentration at 15°S is three times higher compared to the $MeHg^+$ concentration. This result indicates that dimethyl mercury may be the main primary product of biomethylation. Whether monomethyl mercury, as the more stable compound of the two methylated mercury species, is preferably produced from dimethyl mercury by decomposition in the ocean water or is mainly directly produced by different biological species must be proved in further investigations. Up to now, it is known from model experiments with macroalgae under polar conditions that different species of macroalgae produce characteristic fingerprints of the $MeHg^+/Me_2Hg$ distribution. Certain macroalgae are also able to either produce only $MeHg^+$ or $Me_2Hg$.[14] On the other hand, the highest $Me_2Hg$ concentration in the South Atlantic was found at 58°S at the pack-ice border where ATP and TTI did not show elevated values. Here, the dimethyl mercury concentration is about twice as high as that of monomethyl mercury. This result shows that ATP and TTI cannot generally be used as indicators for the biomethylation of mercury although it is well known that bioactivity at the pack-ice border is normally at a relatively high level. A possible explanation for high concentrations of methylated mercury and low ATP and TTI values at the pack-ice border may be the production of these mercury compounds by polar-specific biological species not recorded by the bioindicators applied or the low temperature at this location, which stabilizes the methylated mercury compounds in the ocean water and hinders emission of $Me_2Hg$ into the atmosphere.



## Profiles of methyl mercury compounds in the South Atlantic, South Pacific and Antarctic Ocean (expeditions ANT XI/2 and ANT XII/4)

Figure 6 represents a west-east concentration profile (at latitudes between 41°S and 55°S from Capetown to Punta Arenas) of methyl mercury compounds, which was determined during the expedition ANT XI/2. The biomass indicator chlorophyll-a, measured by Hirch and Bathmann,[17] is also given for comparison. The four different oceanic water fronts, which were crossed during this cruise and where the properties of the ocean water, e.g. its temperature, salinity or nutrient content, changed significantly, are also marked in the figure. These water fronts are the subtropical convergence (A), the sub-Antarctic front (B), the polar front (C) and the Weddell-Scotia confluence (D). At the subtropical con-

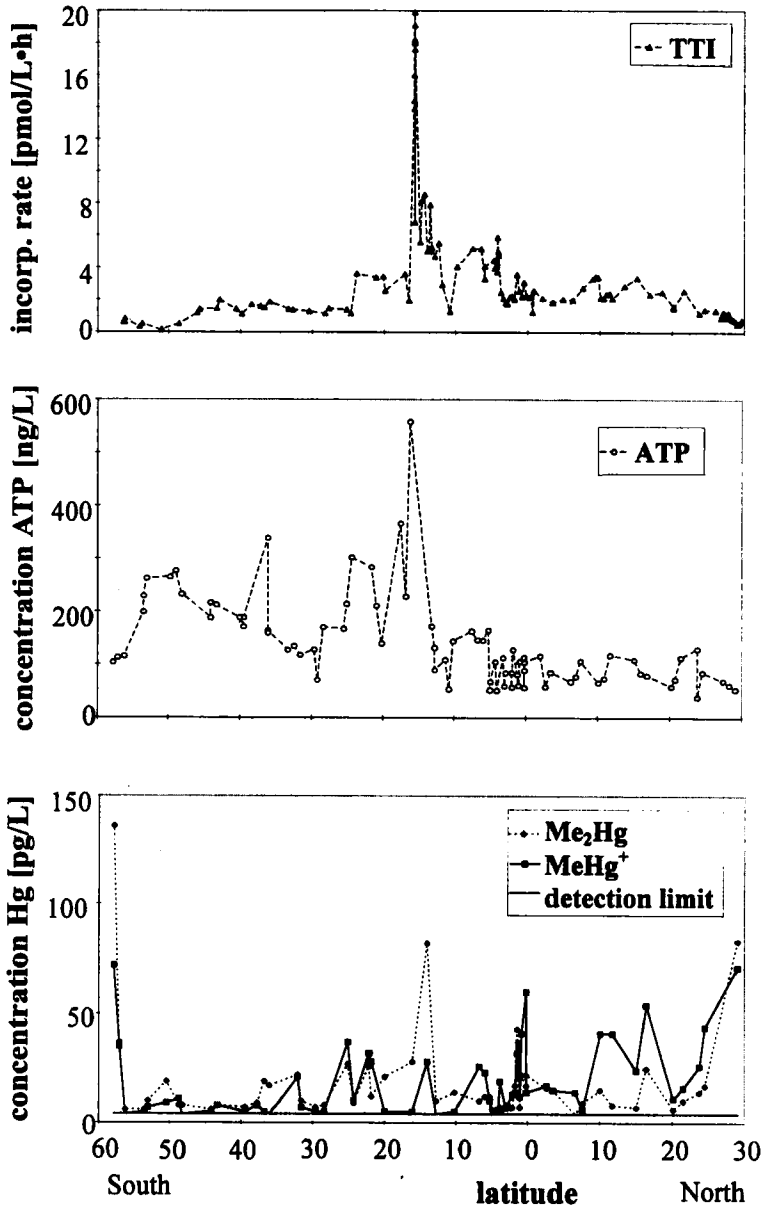


FIGURE 4 North-south concentration profile of $MeHg^+$ and $Me_2Hg$ in surface sea-water samples of the Atlantic Ocean from 30°N to 58°S in correlation with the biomass indicators ATP (adenosine triphosphate) and TTI (tritiated thymidine incorporation). (ATP and TTI data from ref. 15 and 16)

vergence the bioactivity was lower, and therefore also the chlorophyll-a concentration, compared with the situation at the other water fronts. As a consequence, also the concentration of methylated mercury was found to be higher at the sub-Antarctic front, the polar front and the Weddell-Scotia confluence. In the area of the Weddell-Scotia confluence, where the highest chlorophyll-a content was observed, also the highest concentration of $MeHg^+$ and $Me_2Hg$ was detected. In addition, especially high peak concentrations of dimethyl mercury were found at these three water fronts exceeding always the corresponding monomethyl mercury abundance. The phenomenon that $Me_2Hg$ exceeds $MeHg^+$ in cases of high biological activity was also observed during the ANT XI/1 expedition (see Figure 4) and supports the hypotheses that inorganic mercury is preferably bio-methylated to dimethyl mercury under the existing conditions in this part of the South Atlantic.

During expedition ANT XII/4 two concentration profiles in surface sea-water were determined in the South Pacific as well as in the Pacific part of the Antarctic Ocean. The first one is a north-south profile, which is represented in Figure 7 for the methylated mercury data and for the chlorophyll-a concentrations measured by Templin and Bathmann.[18] This figure covers latitudes from 50°S to 70°S and longitudes from 89°W to 98°W (from north-west of Punta Arenas to south-west of Rothera on the Antarctic Peninsula). From oceanographic data it could be derived that the sub-Antarctic front (A) was at 57°S and that the weak polar front was splitted up into a primary (B) and a secondary (C) polar front at 60.5°S and 62.5–64°S, respectively.[19] The pack-ice border (D) was found in the area from 69°S to 70°S. As can be seen from Figure 7, the chlorophyll-a concentration is about a factor of ten lower compared to the situation found for expedition ANT XI/2 (Figure 6). This is due to the different seasons because ANT XI/2 took place in the early Antarctic summer, when increasing bioactivities in the ocean were observed, whereas ANT XII/4 took place during the Antarctic autumn with decreasing biological activities. Therefore, also lower concentrations of methylated mercury species were found in the north-south profile of ANT XII/4 and, in addition, the $MeHg^+$ content mostly exceeded that one of $Me_2Hg$. A real correlation between the chlorophyll-a concentration and the occurrence of methyl mercury compounds cannot be derived from Figure 7, except the fact that the highest contents of $MeHg^+$ and $Me_2Hg$ were found in the area of the pack-ice border with the highest chlorophyll-a concentration.

The second concentration profile for methylated mercury compounds and chlorophyll-a[18], determined during ANT XII/4, represents a west-east direction from 98°W to 68°W (westerly of the Antarctic Peninsula to Rothera on the peninsula) and is shown in Figure 8. This profile can be divided into two areas,

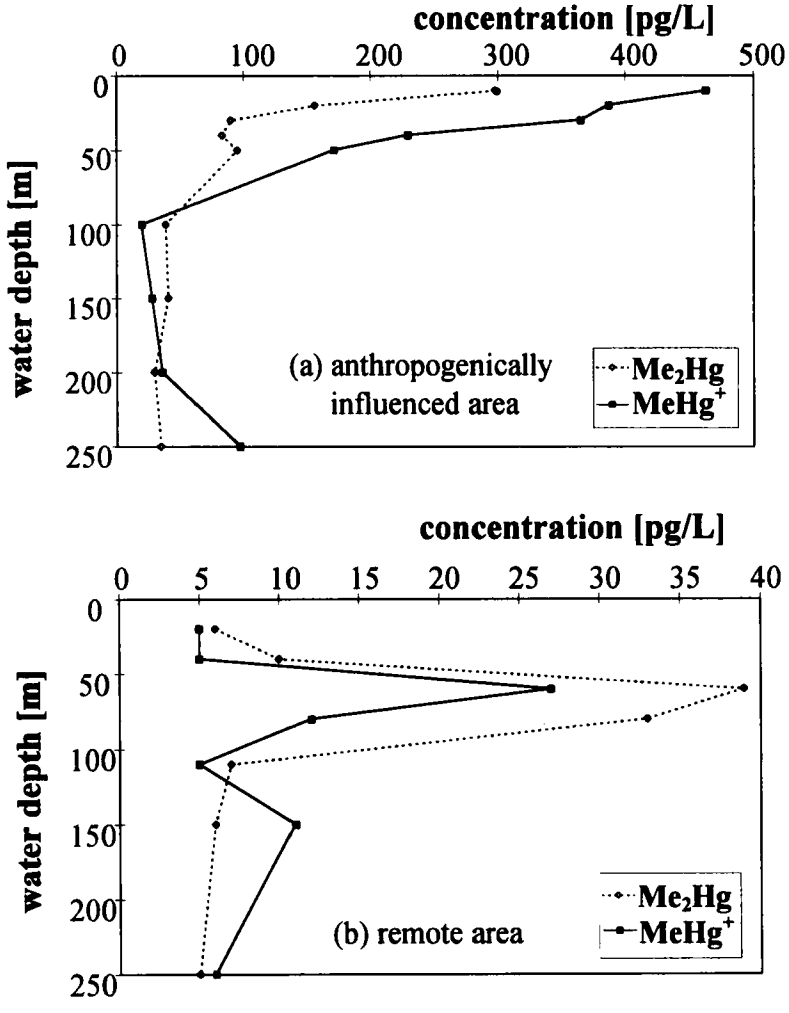


FIGURE 5 Typical depth concentration profile in the ocean of $MeHg^+$ and $Me_2Hg$ for (a) an anthropogenically influenced area (North Atlantic at 47°54'N, 10°20'W) and for (b) a remote area (South Atlantic at 53°30'S, 9°00'E)

characterized by pack-ice (98°W to 84°W) and by a totally closed ice sheet from 84°W to 68°W. In the first area, $Me_2Hg$ as well as $MeHg^+$ could be detected above the detection limit showing low chlorophyll-a concentrations between 0.04 µg/L and 0. 1 µg/L. Contrary to these findings no methylated mercury compounds could be detected above the detection limit in the area of the closed ice sheet, except very small concentrations near the shore of the Antarctic Peninsula.

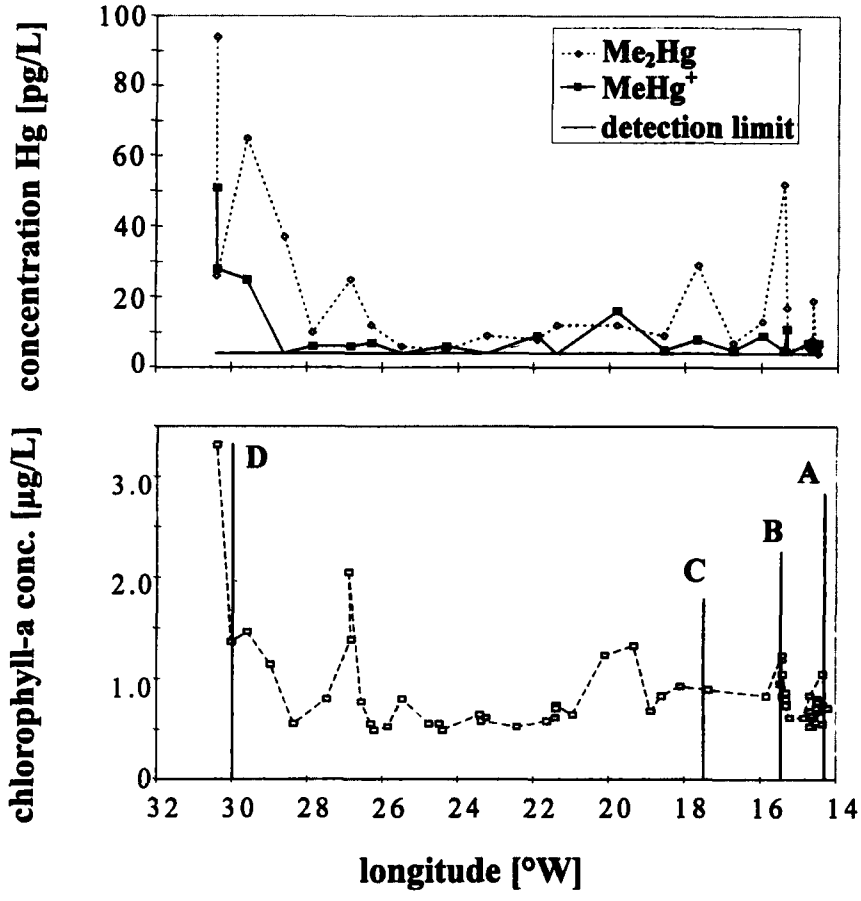


FIGURE 6 West-east concentration profile of $MeHg^+$ and $Me_2Hg$ in surface sea-water samples of the South Atlantic from Capetown to Punta Arenas (14°W to 31°W) in correlation with the biomass indicator chlorophyll-a (marked water fronts: A subtropic convergence, B sub-Antarctic front, C polar front, D Weddell-Scotia confluence). (Chlorophyll-a data from ref. 17)

## West-east profiles of methyl mercury compounds in the Arctic Ocean (expedition ARK X/1)

In Figures 9 and 10 two concentration profiles of both methyl mercury compounds in the Arctic Ocean are presented. The concentration profile in Figure 9 shows the situation at 75°N from 14°W to 16°E and can be divided into four different parts. The pack-ice border extends from 14°W to 8°W. This region is biologically very active,[20] and therefore high concentrations of the methyl mercury compounds were found. The following area is located in the Central Greenland

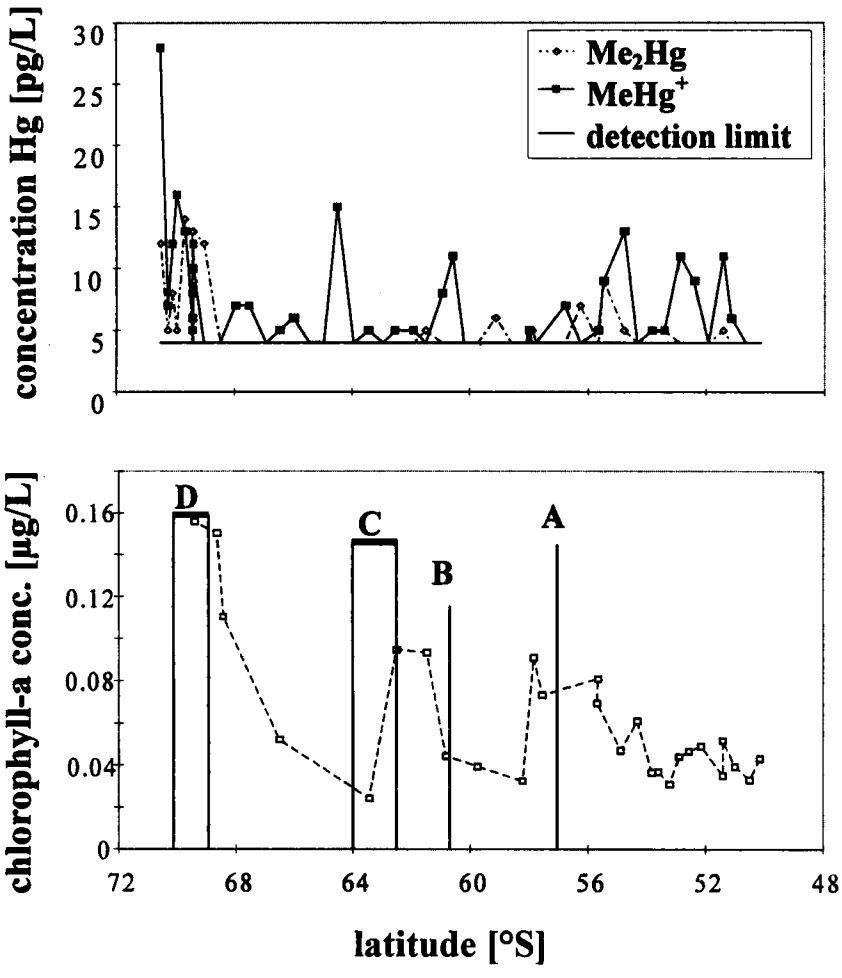


FIGURE 7 North-south concentration profile of $MeHg^+$ and $Me_2Hg$ in surface sea-water samples in the Antarctic Ocean from westerly of Punta Arenas to westerly of the Antarctic Peninsula (50°S to 70°S) in correlation with the biomass indicator chlorophyll-a (marked water fronts: A sub-Antarctic front, B primary polar front, C secondary polar front, D pack-ice border). (Chlorophyll-a data from ref. 18)

Sea which is characterized by low biological productions.[20] The methyl mercury concentrations are therefore relatively low in this area. At about 6°E the Arctic water is mixed with the Atlantic water of the Gulf Stream. As a result of this mixing, the Arctic front is built up and leads to an upwelling water stream, which induces an increased biological growth and high concentrations of methyl mercury compounds. From 14°E to 16°E a similar effect is detected. The water

from the North Atlantic is mixed with shelf water of the Barents Sea. In most cases of this concentration profile monomethyl mercury dominates compared with dimethyl mercury. One reason for that may be the decreasing phytoplakton bloom during the late summer of sampling. As a consequence, the production rate of dimethyl mercury, probably the main primary product of biomethylation, is not at a high level. Therefore, the concentration of the possible degradation product monomethyl mercury exceeds that of dimethyl mercury.

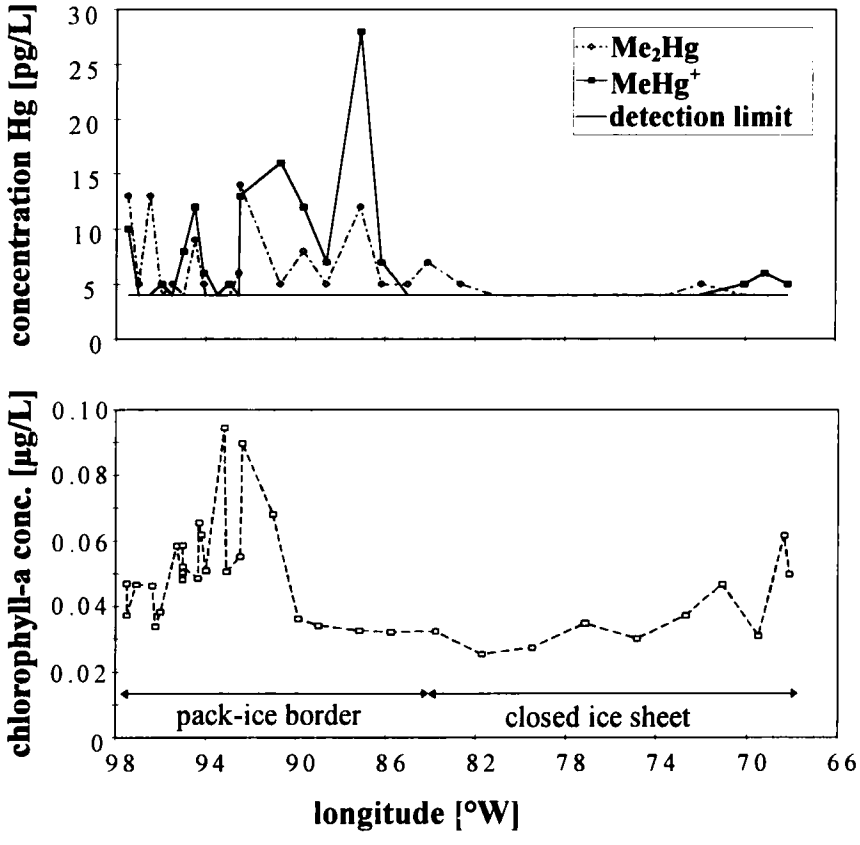


FIGURE 8 West-east concentration profile of $MeHg^+$ and $Me_2Hg$ in surface sea-water samples of the Antarctic Ocean westerly of the Antarctic Peninsula (68°W to 98°W) in correlation with the biomass indicator chlorophyll-a. (Chlorophyll-a data from ref. 18)

The second west-east concentration profile in the Arctic Ocean shows the situation in the Fram Strait at 79°N from 10°W to 0.5°E (Figure 10). In the area of the pack-ice border (4–8°W) relatively high biological activities were found.[20] As a consequence, distinctly increased concentrations of both methylated mer-

cury compounds were measured, which confirms most of the other observations described in this paper.

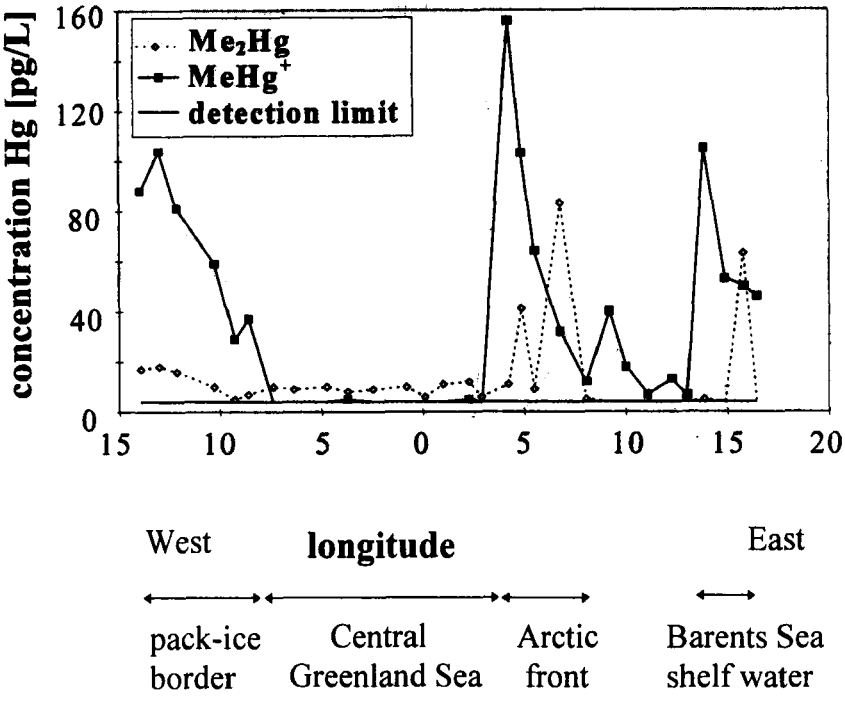


FIGURE 9 West-east concentration profile of $MeHg^+$ and $Me_2Hg$ in surface sea-water samples of the Arctic Ocean at 75°N from 14°W to 16°E

## CONCLUSION

This work presents extensive data on the distribution of methyl mercury compounds in surface ocean water samples, especially for those of the remote areas of the South Atlantic, the South Pacific, the Antarctic and Arctic Ocean. In most cases, the methyl mercury concentrations show positive correlations with biological parameters such as chlorophyll-a and ATP, which indicates their biogenic origin. Even if this is assumed for a couple of years,[21,22] the results of this work in polar and other remote areas still clearly confirm this assumption and, in addition, represent the first set of data for methylated mercury compounds in polar oceans.

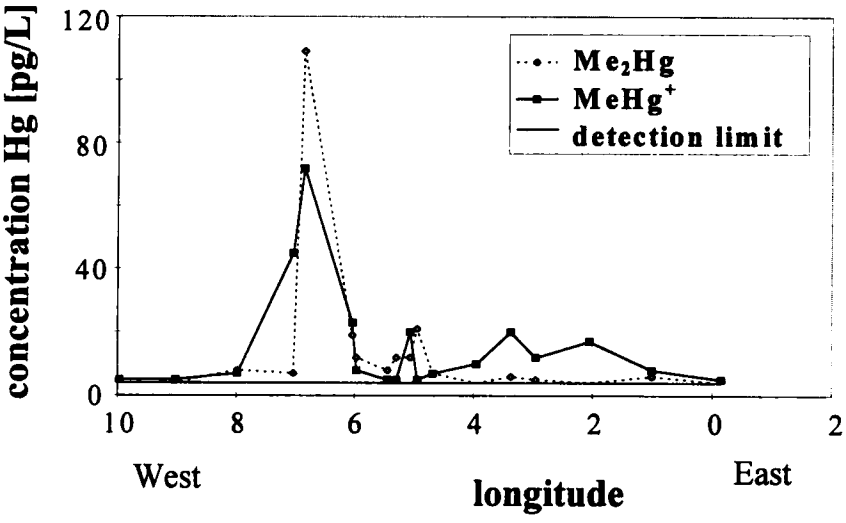


FIGURE 10 West-east concentration profile of $MeHg^+$ and $Me_2Hg$ in surface sea-water samples of the Arctic Ocean at 79°N (Fram Strait) from 10°W to 0.5°E



***Acknowledgements***

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