

Vertical mercury profile in relation to arsenic, cadmium and copper at the eastern North Atlantic ICES reference station

Mercury
Trace metals
Sea water
Atlantic Ocean

Mercur
Métaux en trace
Eau de mer
Océan Atlantique

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ABSTRACT

Mercury (total mercury), arsenic, cadmium, copper and nutrient concentration profiles (fourteen depths) were obtained at the ICES (International Council for the Exploration of the Sea) reference station (46° N; 6° W) in 4 680 m of water in the northeastern Atlantic Ocean.

Concentrations of mercury generally ranged from 0.4 to 10 pM. The main feature of the vertical mercury profile was a broad peak between 150 and 1 500 m. Examination of the mercury profile in relation to water mass structure and comparison with nutrient and other elemental distributions suggested that its shape results from a remobilization of mercury during mineralization of sinking organic detritus combined with its intense scavenging in deeper waters.

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RÉSUMÉ

Répartition verticale du mercure en relation avec celles de l'arsenic, du cadmium et du cuivre à la station de référence du CIEM en Atlantique Nord-Est

Les concentrations en mercure total, arsenic, cadmium, cuivre et en éléments nutritifs ont été mesurées dans l'eau à quatorze profondeurs sur la verticale de la station de référence du Conseil International pour l'Exploration de la Mer (CIEM), située en Atlantique Nord-Est (46°N ; 6°W) et dont la profondeur est de 4 680 m.

La plupart des concentrations en mercure varient de 0,4 à 10 pM et leur profil vertical se caractérise par un pic entre 150 et 1 500 m. L'examen de ce profil en relation avec la structure des masses d'eau et sa comparaison avec les profils obtenus pour les nutriments ou d'autres éléments indiquent que son allure résulte probablement de la mobilisation du mercure lors de la minéralisation de la matière organique particulière dans les couches supérieures combinée avec un enlèvement intense dans les eaux profondes de l'océan.

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INTRODUCTION

Measurements of mercury using ultra-clean techniques (*e. g.* Olafsson, 1983; Dalziel and Yeats, 1985; Gill and Fitzgerald, 1985) have indicated that the concentration levels of this metal in oceanic waters are in the picomolar range, and that most of the data published earlier are of doubtful quality because of contamination problems during sampling, storage and/or analysis.

Gill and Fitzgerald (1988) published the first vertical distributions of mercury in the ocean, and their interpretation has contributed substantially to our understanding of the marine biogeochemistry of mercury. For three stations in the Northwestern Atlantic, the profiles obtained were interpreted in terms of lateral transport of mercury-enriched waters from higher latitude or from contact with margin sediment. Recently, Mason and Fitzgerald (1991) point out that the dissolution of particulate in the low oxygen region is the main supply of reactive mercury (easily reducible mercury forms at pH 1) for sub-thermocline waters. We report here the vertical distribution of total mercury concentrations at a reference station of the International Council for the Exploration of the Sea (ICES) in the Eastern Atlantic and discuss the behaviour of mercury in relation to hydrography and distributions of nutrients, arsenic, cadmium and copper. We propose that the recycling of organic matter in the upper layers, together with intense scavenging in deep waters, are responsible for the observed mid-depth maximum of mercury in the water column.

METHODS

The station occupied is located in the abyssal plain off the Bay of Biscay (46° N; 6° W) in 4 680 m of water. This station was selected by ICES because of the relative stability of the hydrographic conditions and the vicinity of the ICES baseline survey areas (Topping and Bewers, 1984).

Table

Analytical data from the ICES reference station (46°N; 06°W).

Résultats analytiques à la station de référence du CIEM (46°N ; 6°O).

Depth (m)	Temperature (°C)	Salinity (10 ⁻³)	Phosphate (µM)	Nitrate (µM)	Cadmium (nM)	Copper (nM)	Arsenic (nM)	Mercury (pM)
0	15.25	35.49	0.13	0.5	0.09	2.50	22	< 1.0
10	14.89	35.59	0.13	0.5	0.05	1.86	20	9.0
20	14.89	35.59	0.13	0.8	0.06	2.00	17	4.2
40	14.89	35.56	0.15	0.8	0.06	2.00	17	4.2
75	14.37	35.57	0.31	4.3	0.09	1.72	18	4.4
150	11.58	35.60	0.53	8.6	0.12	1.37	21	4.2
300	11.18	35.58	0.63	10.2	0.13	1.57	23	8.6
500	10.76	35.55	0.73	11.2	0.16	1.27	24	9.9
800	10.25	35.70	1.03	17.1	0.20	1.42	26	19.1
1 000	9.72	35.74	1.08	18.5	0.21	1.27	21	7.7
1 500	5.87	35.27	1.20	19.1	0.22	-	-	6.0
2 000	3.90	35.05	1.31	19.9	0.26	1.99	21	3.9
2 500	3.14	35.00	1.38	20.9	0.28	2.33	21	4.2
3 000	2.75	34.96	1.50	21.2	0.32	2.53	22	4.1

Samples were collected on 28 October 1987 between the surface and 3 000 m during a cruise on the R/V *Noroit*. The surface water sample was collected by hand from a rubber boat 200 m upwind from the main ship directly into an acid-cleaned teflon (FEP) storage bottle. Deep samples were collected using two 5L teflon-coated GO-Flo bottles attached to a new stainless steel hydrowire deployed from a methanol cleaned winding drum. The two samplers were cleaned, assembled and sealed in polyethylene bags in a land-based clean room. Samples were collected in two-bottle casts starting with the two bottom depths (3 000 and 2 500 m) and moving upward. The GO-Flo bottles were carried inside a clean room (class 1 000) container. Water was drained from the samplers into acid-washed 500 ml teflon (FEP) bottles for subsequent determination of arsenic and mercury. The samples were stored unfiltered, acidified to pH 0.9 (addition of Suprapur HCl, Merck) and were kept tightly closed and wrapped in plastic bags. The analyses were performed within two months of sampling.

Sub-samples were also drained from the GO-Flo for other trace element and nutrient determinations; they were stored in acid-cleaned polyethylene at pH 1.6 (addition of Suprapur HCl) for trace elements and frozen in polyethylene bottles for nutrients.

The analytical procedure is described elsewhere (Cossa and Noël, 1987) and includes a bromination step to convert organomercury species into SnCl₂ reducible mercury, a gold amalgamation step and finally detection by cold vapour atomic absorption spectrometry. This procedure is designed to measure all mercury forms (total mercury) present in the water. The precision and the detection limit have been estimated as 20 % and 1 pM respectively. The reliability of this technique has been demonstrated in two recent international intercalibration exercises (Berman and Boyko, 1987; Cossa and Courau, 1990).

Cadmium and copper were determined by the chelation extraction method described by Danielsson *et al.* (1982). Arsenic (III and V) was determined by hydride generation

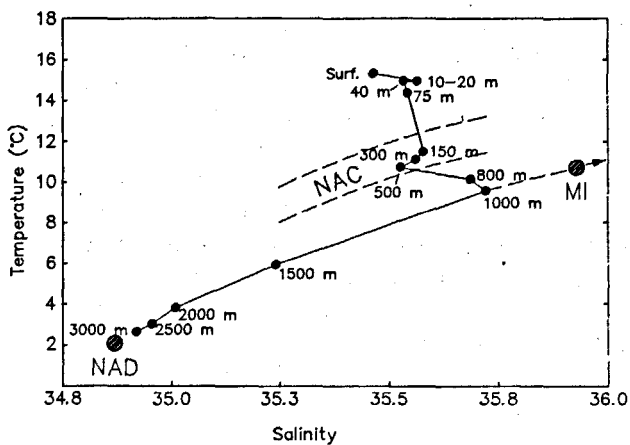


Figure 1

T-S diagram at the ICES reference station (46° N; 6° W).

Diagramme T-S à la station de référence du CIEM (46° N; 6° O).

according to Andreae (1977). Phosphate and nitrate were analysed using the standard colorimetric methods.

RESULTS AND DISCUSSION

Values of salinity, temperature, phosphate, nitrate, arsenic, cadmium, copper and mercury measurements are given in the Table.

Hydrographical data

The T-S diagram (Fig. 1) is typical of the water masses found in this area (Mamayev, 1975; Fruchaud-Laparra *et al.*, 1976 a). Sub-surface waters (10-75 m) have salinities between 35.56×10^{-3} and 35.59×10^{-3} and temperatures from 14° to 15° C; surface water (0 m) is less saline and warmer. Below the main thermocline, located around 100 m, the North Atlantic Central Water (NACW) was sampled at 150, 300 and 500 m. Between 500 m and 1 500 m a sharp salinity gradient indicated the asymmetrical mixing of Mediterranean Intermediate Water (MIW) (Mamayev, 1975). The maximum of the influence of MIW is observed at 1 000 m, with mixing evidence visible from 800 to 1 500 m. At greater depths, salinities and temperatures (2 000-3 000 m) are typical of the North Atlantic Deep and Bottom Water (NADW).

Nutrients, arsenic, cadmium and copper data

The nutrient profiles (Fig. 2) showed that concentrations typically increased from the surface to the deep water with two main regeneration zones: one from the surface to 800 m and the other from 800 m to 3 000 m. The maximum of nutrient regeneration is located at 800 m where the minimum in dissolved oxygen was previously observed at the same station (Fruchaud-Laparra *et al.*, 1976 b).

Cadmium is known to have "nutrient-like" behaviour in the ocean (Bruland, 1983). At the present station it exhibited a

strong correlation with phosphate ($[Cd] \text{ nM} = 0.17 \pm 0.01 [PO_4^{2-}] \mu\text{M} + 0.03 \pm 0.01$; $r = 0.99$, $p \geq 0.0001$). The vertical distribution is a function of biological uptake and release and of the rate of vertical mixing between the depleted surface waters and the enriched deeper waters (Fig. 3).

A mid-depth minimum in the copper distribution (Fig. 3) is thought to result from a surface input coupled with regeneration near the ocean floor (Bruland, 1983). The concentration values obtained here agree well with the data published by Bruland and Franks (1983) for the Western North Atlantic. Shelf waters have a much higher copper concentration than oceanic surface water (Kremling, 1985) and this fact suggests that the continental influence on this profile is small.

The usual "nutrient-like" behaviour of arsenic (Andreae, 1986), is indicated in this profile on Figure 3 by a sub-surface depletion. The concentration range is very consistent with earlier data for the Atlantic (Statham *et al.*, 1987; Middelburg *et al.*, 1988). However, an atypical high arsenic concentration level, with a As/PO₄ ratio (25×10^{-3}) out of the range usually encountered ($8-20 \times 10^{-3}$), is found at 800 m. This may be due to a contamination of this sample.

From Figure 3, there is no obvious indication of a particular influence of MIW (the maximum proportion of which is located at 1 000 m, Fig. 2) on the metal profiles.

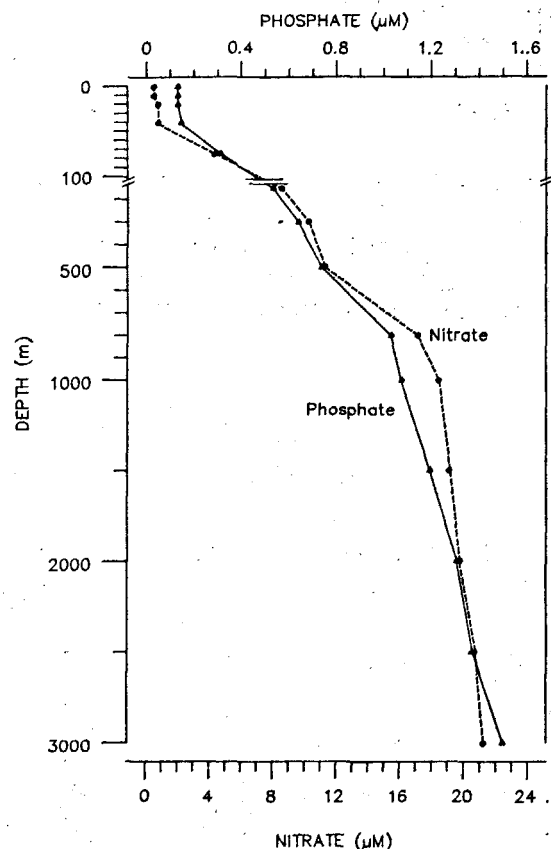


Figure 2

Phosphate and nitrate profiles at the ICES reference station (46° N; 6° W).

Profils de phosphate et de nitrate à la station de référence du CIEM (46° N; 6° O).

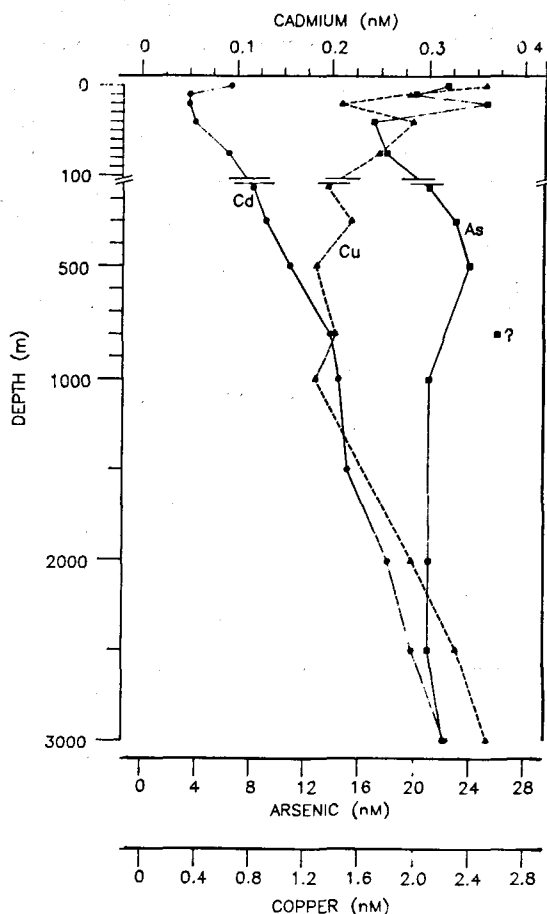


Figure 3

Arsenic, cadmium and copper profiles at the ICES reference station (46° N; 6° W).

Profils d'arsenic, de cadmium et de cuivre à la station de référence du CIEM (46° N; 6° O).

Total mercury data

All concentrations except that at 800 m ranged between < 1 and 10 pM (Table). These levels are similar to those found by Gill and Fitzgerald (1988) for the Northwest Atlantic (1.6 - 11 pM), and by Olafsson (1983), Dalziel and Yeats (1985) and Fileman and Harper (1989) for the Central North Atlantic Ocean (1.4 - 11 pM). The concentration measured at 800 m (19.1 pM) is quite high. The sub-sample analysed for mercury at 800 m came from the same FEP storage bottle for which an exceptional high arsenic level was found; although the possibility for a high true value cannot be ruled out, the suspicion for a contamination of this sample, as suggested for arsenic, is justified for mercury.

The main feature of the vertical profile was a broad peak between 150 and 1500 m (Fig. 4). This maximum in mercury concentrations crossed NACW and MIW, while the surface and NADW were characterized by lower concentrations. Mixed layer concentrations averaged 4.2 ± 2.5 pM, levels similar to those found by Gill and Fitzgerald (1988) near Bermuda. Such concentrations are higher than those measured at the same depth in the Pacific Ocean (Gill and Fitzgerald, 1988). Below 2000 m, typically NADW, mercury concentrations are also higher than in the Pacific

Ocean, where Gill and Bruland (1987) measured between 0.8 and 1.3 pM below 2000 m. These data suggest that atmospheric input, the main source of mercury for oceanic waters (Fitzgerald, 1989) influences not only the concentrations in the surface water but also those of the deep and bottom waters. Schaule and Patterson (1983) suggested a similar scenario for lead, another trace element with a predominantly atmospheric source.

While considering the atmosphere as the main source of mercury for oceanic waters, a removal mechanism should be evoked to explain the low mercury concentrations in surface waters compared with underlying waters. The return to the atmosphere of elemental mercury formed as the result of biomediated reduction has been suggested (Kim and Fitzgerald, 1986); nevertheless this process probably does not provide the sole explanation. Recently, Mason and Fitzgerald (1991) suggest, from the maximum in mercury they observed in the thermocline region in the Pacific Ocean, that regeneration and release of dissolved mercury from particulate matter is occurring. Indeed, Wallace *et al.* (1982) and Lu *et al.* (1987), using controlled experimental enclosures (Cepex programme), demonstrated that mercury was removed by biogenic sinking particles and was released from particles after a maximum in productivity. This suggests that mercury is involved in the organic matter cycle in the ocean. Despite this observation no study has convincingly demonstrated a remobilization of mercury with mineralization of organic sinking detritus in a natural environment.

The maximum found at intermediate depth at the ICES reference station indicates that a mercury source exists at these

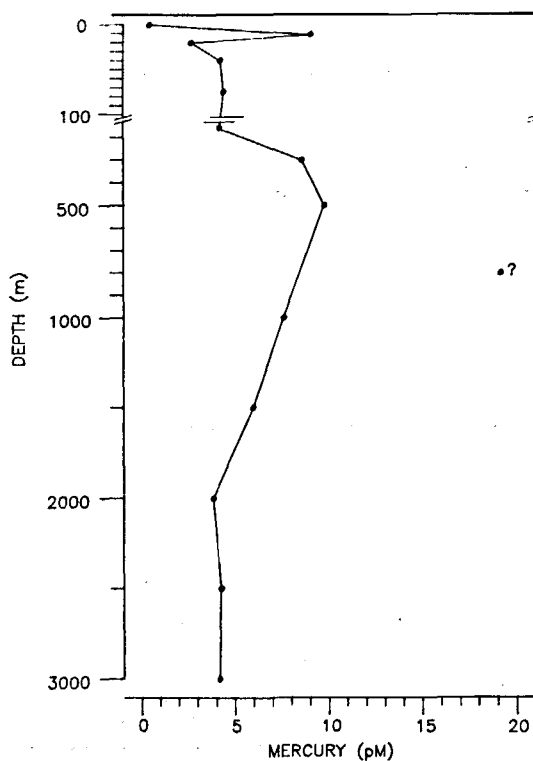


Figure 4

Total mercury profile at the ICES reference station (46° N; 6° W).

Profil de mercure total à la station de référence du CIEM (46° N; 6° O).

levels and that this input is not related to a particular water mass. Indeed, the maximum of mercury concentration, located within the depth range influenced by MIW, does not coincide with the water depth (1 000 m) where the maximum of MIW characteristics are present. Furthermore, the peak in mercury concentration occurs across the boundary of NACW and MIW. Consequently, it appears to be related to a process occurring within these water masses. Mineralization of sinking organic detritus, which contributes to the sharp gradient in nutrient profiles between 0 and 800 m (Fig. 2), is the most likely mechanism. Indeed, the mercury and phosphate concentrations in the main regeneration zone (including the data set between 0 and 800 m), are significantly correlated ($r = 0.82$, $n = 9$) with a regression coefficient of 13.8 ± 3.7 (pM/ μ M) can be calculated. A relationship of this type is also obtained for cadmium (nM) and phosphate (μ M) for ($r = 0.97$, $n = 9$) within the same water layer. The calculated slope for cadmium and phosphate (0.15 ± 0.01 nM/ μ M) is consistent with slope values compiled by Yeats (1988) for Atlantic waters. This suggests that the increase in mercury concentrations between the surface and 800 m can be explained by a remobilization of this element during mineralization of sinking organic detritus. In order to check the rationale of this hypothesis, we calculated the flux of mercury (F) away from 800 m downward and upward: $F = K \cdot dC/dz$ with C the mercury concentration ($\text{pmol} \cdot \text{m}^{-3}$), z the depth (m) and taking the coefficient of diffusive mixing $K = 10^{-5} \text{ m}^2 \text{ s}^{-1}$. From the Figure 3 profile, F is estimated to be $83 \text{ pmol} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$. There is no data available on the particulate mercury flux from the euphotic zone downward in the studied area to verify whether this F flux can be sustained. However, the high productivity of this zone ($1.9 \text{ g C} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ according to Tréguer *et al.*, 1979) and the range of available mercury fluxes estimated by Lu *et al.* (1987) on the basis of sediment trap measurements for Saanich inlet ($1240\text{-}3280 \text{ pmol} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$) indicate that remobilization of mercury during particulate organic matter degradation is reasonable as the main mechanism to explain the intermediate mercury peak.

Intense scavenging of mercury in deeper waters as suggested by Gill and Fitzgerald (1988) would maintain relatively low levels of mercury in the deep ocean. Differences in the rates of regeneration and removal, and in the rate of mixing of water masses, could explain the decrease in mercury concentrations between 800 and 2 000 m.

Alternatively, the presence of a mercury peak at intermediate depth can be explained, as suggested by Gill and Fitzgerald (1988), by advective transport (*via* mixing along isopycnals) of higher latitude surface waters and/or lateral advection of waters which have been enriched in mercury by contact with margin sediments where diagenetic reactions may remobilize mercury. The former hypothesis is unlikely because advection of surface water at 800 m would result in lower phosphate and cadmium concentrations. The latter may adequately explain the high mercury concentration at 500 m where the minimum of salinity (Fig. 1.) is a tracer of waters cascading along the continental shelves of the Irish and Celtic seas (Fruchaud-Laparra *et al.*, 1976 a). However, the copper profile (Fig. 3) exhibits a typical minimum at intermediate depth, arguing against the possibility of any major influence of metal mobilization from margin sediment on the metal profiles observed at that station. Horizontal transport combined with remineralization may, however, contribute to form the mercury maximum. Additional profiles would be necessary to test this hypothesis.

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