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How changes in biological production affect methylmercury vertical profiles in an open ocean environment, the Ligurian Sea (Northwestern Mediterranean)

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Abstract:

Methylmercury was measured monthly for 16 months at 12 depths in a 2350m deep-water column of the Ligurian Sea (Northwestern Mediterranean). In the same time proxies for the biological activity were also monitored (dissolved oxygen, chlorophyll a, nutrients, etc.). Methylmercury concentrations varied within the femtomolar range (0.31±0.17pM, n=189) with the lowest values at surface increasing with depth up to the phosphate maximum and oxygen minimum zone (200-400m). While concentrations in the upper 100 m never exceeded 0.40pM, highest concentrations where encountered after phytoplankton blooms in a highly stratified water column, with a maximum of 0.82pM at 400m.

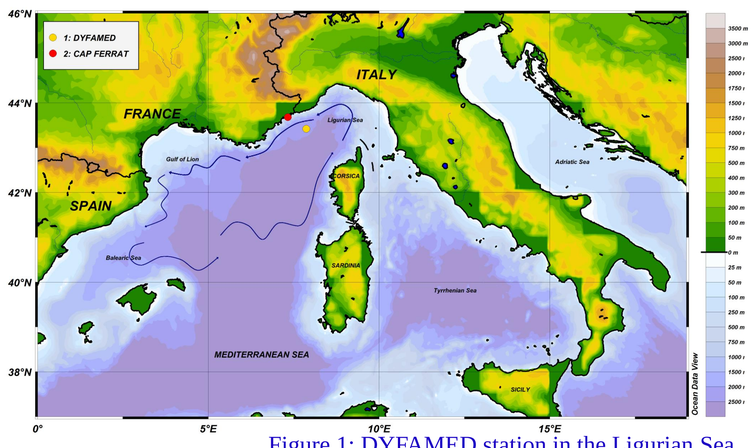

Figure 1: DYFAMED station in the Ligurian Sea

Studied site

The sampling location (DYFAMED) is located between the French Riviera and the Corsica (Fig. 1). This off-shore station is considered as free from direct riverine influence and basically influenced by atmospheric inputs (Marty and Chiavérini, 2002).

Results

Methylated mercury (MeHg=MMHg+DMHg) concentrations ranged from below 0.04 to 0.82pmol·L^{-1}. The data presents a log-normal frequency distribution with a geometrical mean of 0.31±0.17pmol·L^{-1} (n=189). MeHg concentrations in the surface mixed-layer (ML) remained low throughout the year (<0.2pmol·L^{-1}). Highest concentrations where found at intermediate depths (~400m) within the oxygen minimum zone, with a decreasing trends towards the sea bed **(Fig. 2).** MeHg concentrations varied seasonally with lowest values in winter and highest after blooming periods.

Table 1: MeHg / PO_4^{3-} relationship for the upper 600m

[MeHg] (pM) =	**x [PO_4^{3-}]** (µM) **+ b**	**R^2**
July 07	0.61 [PO_4^{3-}] + 0.25	0.37
September 07	0.98 [PO_4^{3-}] + 0.16	0.80
October 07	1.43 [PO_4^{3-}] + 0.16	0.82
November 07	0.72 [PO_4^{3-}] + 0.16	0.28
December 07	0.81 [PO_4^{3-}] + 0.03	0.69
January 08	0.78 [PO_4^{3-}] + 0.09	0.87
March 08	1.16 [PO_4^{3-}] – 0.03	0.94
April 08	0.80 [PO_4^{3-}] + 0.06	0.90
May 08	0.90 [PO_4^{3-}] + 0.06	0.94
June 08	0.95 [PO_4^{3-}] + 0.09	0.88
July 08	0.86 [PO_4^{3-}] + 0.10	0.80
August 08	0.76 [PO_4^{3-}] + 0.09	0.88
September 08	0.74 [PO_4^{3-}] + 0.10	0.93
October 08	0.77 [PO_4^{3-}] + 0.12	0.83
November 08	0.64 [PO_4^{3-}] + 0.06	0.82
January 09	0.72 [PO_4^{3-}] + 0.03	0.99

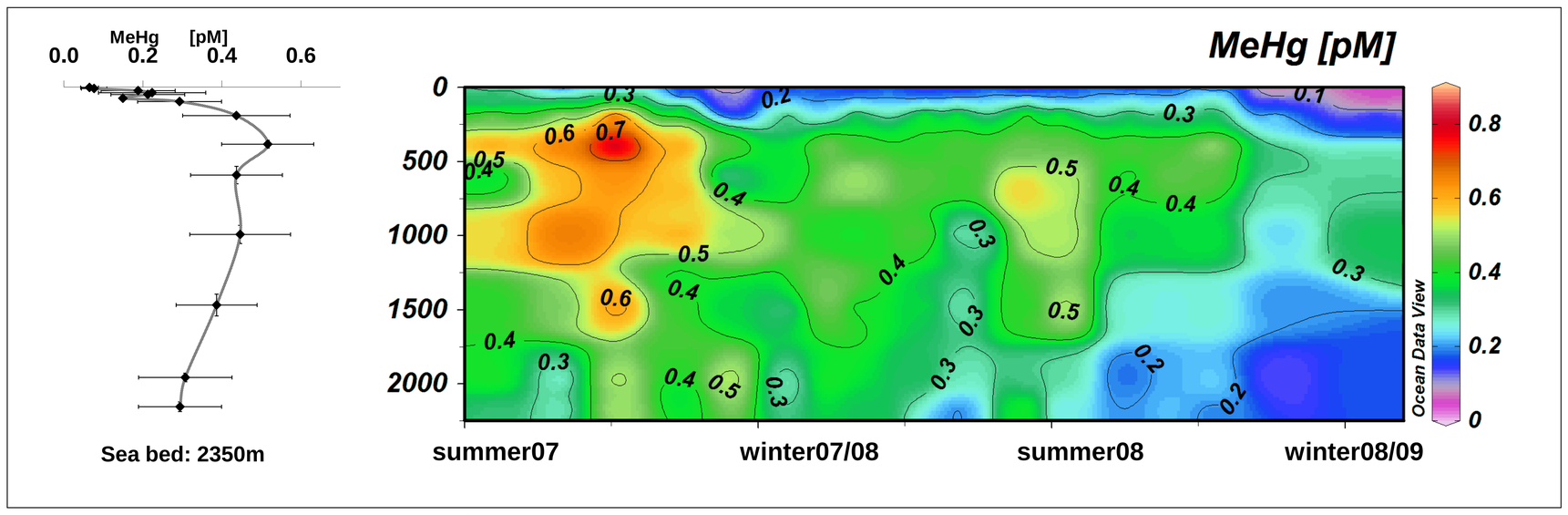

Figure 2: $MeHg_T$ vertical distributions (0 – 2200m) from July 2007 till January 2009

Sources of methylmercury

All vertical MeHg distributions exhibited nutrient-like profiles within the first 600m and peaked within the oxygen minimum layer (Figures 2 and Table 1). This pattern, already observed in other regions of the Mediterranean Sea (Cossa et al., 2009) and in the Northern Pacific (Sunderland et al., 2009), would indicate two processes occurring during the downward mineralization of the organic matter (OM): (i) the release of the MeHg accumulated by the phytoplankton in surface waters, and (ii) the microbiological methylation of the inorganic mercury released during the during the OM degradation. According to Monperrus et al. (2007) Hg methylation is taking place in oxic surface seawater, with the methylation rate varying along with both phyto- and bacterio-plankton abundance and activity. The slope of the relationship between MeHg and PO_4^{3-} within the regeneration zone, which peaked after plankton blooms (in spring and autumn) would reflect the intensity of the of methylation during the OM regeneration process (Table 1).

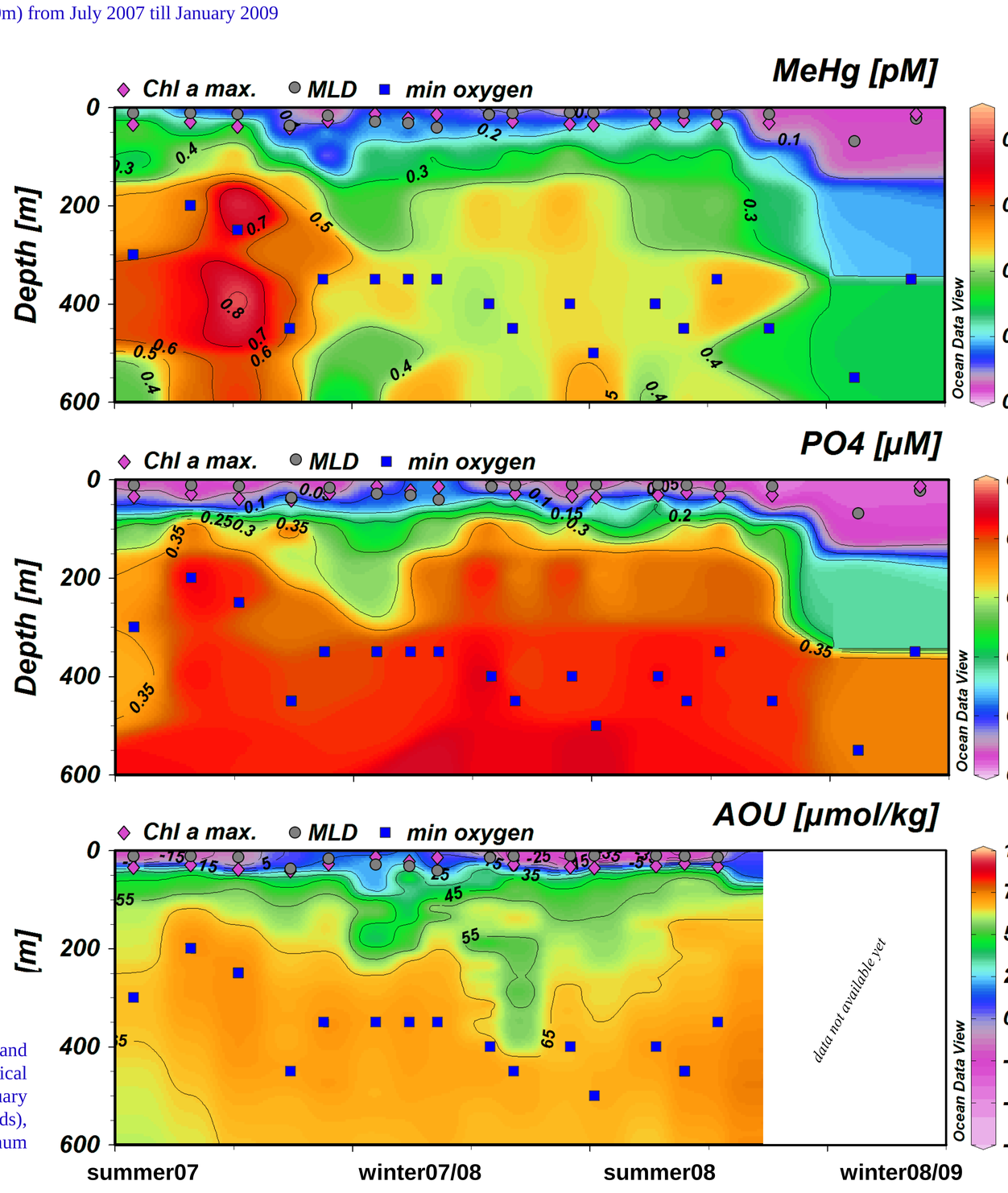

Figure 3 (right): MeHg, orthophosphate and apparent oxygen utilization (AOU) vertical distributions (0-600m) from July 2007 till January 2009; chlorophyll a maximum depth (diamonds), mixed layer depth (MLD; circles) and minimum oxygen depth (squares)

Sampling and analyses: Water column profile samples were collected using externally-closing, Teflon-lined Niskin-1010X samplers deployed on an Carousel water sampler (Sea Bird SBE32). Sixteen (16) monthy events were sampled from July 2007 till January 2009, with 12 samples collected between the surface and 2200 m. Sub-samples for mercury speciation measurements were immediately withdrawn into acid-cleaned Teflon (FEP) bottles following ultraclean sample handling protocols, and were immediately acidified with HCl (0.4%, Suprapur, Merck). All Teflon bottles were hermetically sealed, double-wrapped in polyethylene bags, and kept in the dark at +4°C. MeHg was measured on unfiltered acidified samples as volatile monomethylmercury hydride, by purge and cryo-trapping gas chromatography, and detected as elemental Hg vapor by atomic fluorescence spectrometry (Tekran, Model 2500). The analytical protocol is derived from Stoichev et al. (2004). The separation column used is a glass tube filled with Chromosorb W/AW-DMCS impregnated with 15% OV-3. Analytical repr oducibility was better than 15%. Detection limit was 0.04pM. The accuracy was checked using a certified reference material (ERM-AE670) from IRMM (European Commission).

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