A Michaelis–Menten type equation for describing methylmercury dependence on inorganic mercury in aquatic sediments

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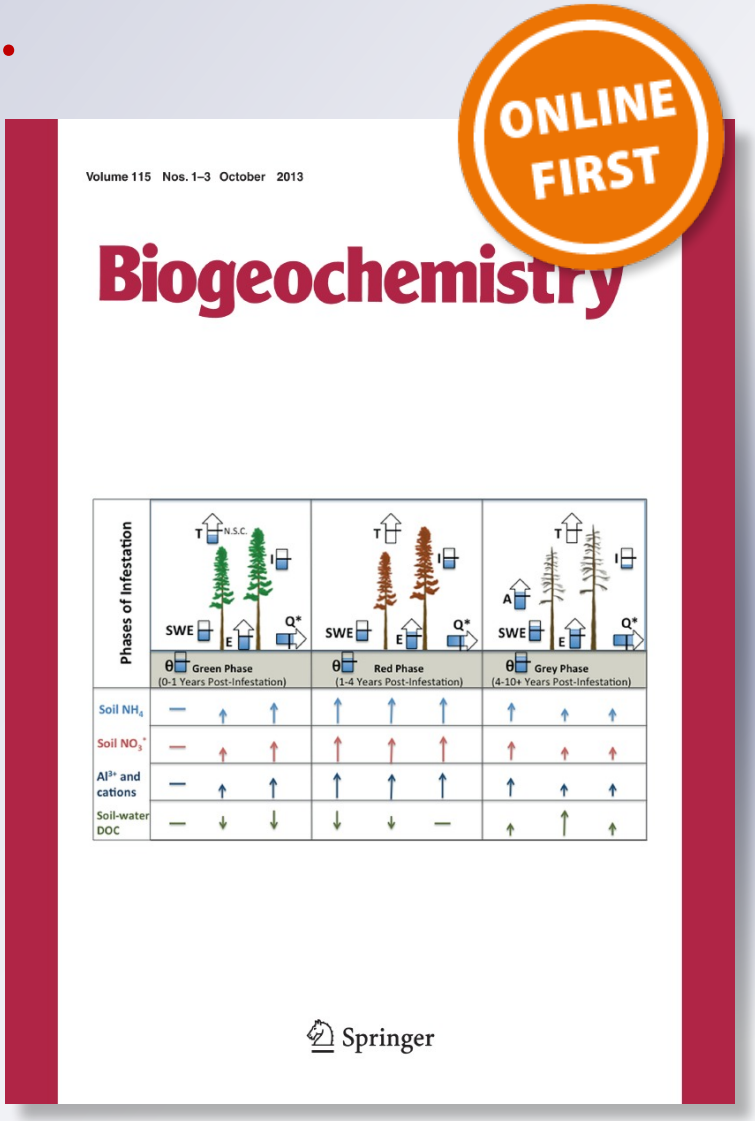

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Abstract Methylation of mercury (Hg) is the crucial process that controls Hg biomagnification along the aquatic food chains. Aquatic sediments are of particular interest because they constitute an essential reservoir where inorganic divalent Hg (Hg^{II}) is methylated. Methylmercury (MeHg) concentrations in sediments mainly result from the balance between methylation and demethylation reactions, two opposite natural processes primarily mediated by aquatic microorganisms. Thus, Hg availability and the activity of methylating microbial communities control the MeHg abundance in sediments. Consistently, some studies have reported a significant positive correlation between MeHg and Hg^{II} or total Hg (Hg_T), taken as a proxy for Hg^{II}, in aquatic sediments using enzyme-catalyzed methylation/demethylation mechanisms. By compiling 1,442 published and unpublished Hg_T–MeHg couples from lacustrine, riverine, estuarine and marine sediments covering various environmental conditions, from deep pristine abyssal to heavily contaminated riverine sediments, we show that a Michaelis–Menten type relationship is an appropriate model to relate the two parameters: $MeHg = aHg_T/(K_m + Hg_T)$, with $a = 0.277 \pm 0.011$ and $K_m = 188 \pm 15$ ($R^2 = 0.70$, $p < 0.001$). From K_m variations,

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which depend on the various encountered environmental conditions, it appears that MeHg formation and accumulation are favoured in marine sediments compared to freshwater ones, and under oxic/suboxic conditions compared to anoxic ones, with redox potential and organic matter lability being the governing factors.

Keywords Mercury · Methylmercury · Aquatic sediment · Methylation · Demethylation

Introduction

Methylmercury (MeHg), mercury (Hg) most toxic form, bioconcentrates in organisms and biomagnifies along the aquatic food chains (Clarkson and Magos 2006). Although MeHg concentrations in sediments can be affected by exchanges with the water column, the main controlling factor of these concentrations appears to be the balance between Hg^{II} in situ methylation and MeHg demethylation reactions, two opposite natural processes primarily mediated by aquatic microorganisms (e.g., Ullrich et al. 2001; Barkay et al. 2011; Gilmour et al. 2011; Yu et al. 2012). Despite some early laboratory experiments which suggested that Hg^{II} methylation results from the activity of many aerobic and anaerobic microorganisms (Jensen and Jernelöv 1969; Vonk and Sijpesteijn 1973), more recent researches showed that methylation capacity in aquatic sediments is limited to anaerobic bacteria, including sulfate-reducing bacteria (SRB) (Compeau and Bartha 1984, 1985; Choi et al. 1994; Baldi 1997), iron-reducing bacteria (IRB) (Fleming et al. 2006; Kerin et al. 2006; Yu et al. 2012) and methanogens (Hamelin et al. 2011). Furthermore, environmental incubations also suggested that SRB and IRB are the main mercury methylators in natural environments (Gilmour et al. 1992, 2011; Yu et al. 2010, 2012; Acha et al. 2012), with SRB being the dominant community (Choi et al. 1994; Baldi 1997; Pak and Bartha 1998; Yu et al. 2010). On the other hand, MeHg demethylation results from numerous types of microorganisms in both aerobic and anoxic environments (Oremland et al. 1991; Dahlberg and Hermansson 1995; Pearson et al. 1996; Marvin-Dipasquale and Oremland 1998; Marvin-Dipasquale et al. 2000), either by reductive or oxidative demethylation (Barkay et al. 2011; Mason 2012). In oxidative demethylation, active in SRB and methanogens, MeHg is converted into Hg^{II}, whereas in reductive demethylation, more extensively distributed throughout microbial communities, MeHg is converted into Hg^0.

For bacterial Hg^{II} methylation, Parks et al. (2013) recently reported a two-gene cluster *(HgcA* and *HgcB)*, suggesting a common Hg pathway in all methylating bacteria hitherto sequenced, including SRB, IRB and methanogen strains. Radiolabelled experiments suggested that a methyl group of methyltetrahydrofolate, from the acetyl-CoA pathway, is transferred to *HgcA* as CH_3^+, consistently with the enzyme-catalyzed methylation pathway earlier proposed by Choi et al. (1994). For MeHg demethylation, multiple enzymatic pathways coexist. The oxidative demethylation, primarily producing CO_2, seems ubiquitous in anaerobic sediments (Oremland et al. 1991), whereas reductive pathway, producing mainly CH_4 (via the organomercurial-lyase pathway, Begley et al. 1986), dominates in aerobic sediments or under anaerobic incubations of highly contaminated sediments (Marvin-Dipasquale et al. 2000; Schaefer et al. 2002; Segade et al. 2010).

All these proposed pathways suggested that an enzymatic model between MeHg net formation and its substrate concentration (Hg^{II}) should be shared in every sedimentary situation. Indeed, Gilmour et al. (2011) found a strong positive relationship between MeHg production and the log of the total Hg concentration obtained in a controlled experiment involving a SRB, *Desulfovibrio desulfuricans.* King et al. (1999) also found a nonlinear relationship between rates of MeHg formation as a function of Hg^{II} added in sediment slurries, consistent with a first-order Michaelis–Menten model. Besides the results of these experimental approaches, several field studies converged to find significant positive relationships between Hg^{II} or Hg_T, and MeHg in freshwater, brackish and marine sediments (e.g., Benoit et al. 2003; Hammerschmidt and Fitzgerald 2006; Drott et al. 2008; Marvin-Dipasquale et al. 2009; Gilmour et al. 2011). These empirical relationships also suggested that net MeHg production in aquatic sediments is limited by Hg^{II} availability, if Hg_T is assumed as a proxy for Hg^{II} substrate for methylation, which is reasonable since

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MeHg, in most cases, represents less than 1 % of sedimentary Hg_T. Testing various substratum including cinnabar, metacinnabar, Hg^{II} bound to mackinavite or organic matter (OM), Jonsson et al. (2012) reported Hg methylation rates spanning over two orders of magnitude, increasing with Hg^{II} dissolution or desorption from solids. Besides mobilization from solid, OM was also suggested as a key-parameter of Hg sediment-water partitioning and bioavailability, which seems to constrain MeHg/Hg_T in surface sediments (e.g., Sunderland et al., 2006; Hammerschmidt and Fitzgerald, 2006; Schartup et al., 2013). Lastly, large differences between estimations of Hg methylation rates exist, depending on environmental conditions, which are not directly related to Hg^{II} bioavailability, but rather to changes in the present microbial communities (Ranchou-Peyruse et al. 2009; Segade et al. 2010; Mason 2012; Hsu-Kim et al. 2013).

In order to further examine the environmental conditions that control net Hg methylation and limit MeHg accumulation in aquatic sediments, we propose the use of a model resembling Michaelis–Menten kinetics synthesizing the enzymatic methylation and demethylation reactions. We thus applied this type of model to 1,442 MeHg/Hg_T couples, collected in scientific literature or from our unpublished works. The gathered data cover sedimentary environments from surface to deep layers including abyssal, coastal, lagoonal, estuarine, lacustrine and riverine sediments, and range from pristine to heavily polluted areas and from aerobic to sulfidic environments. It appears that a Michaelis–Menten equation significantly ($p < 0.001$) relates MeHg to Hg_T concentrations accordingly to the converging hypotheses of Benoit et al. (2003), Drott et al. (2007, 2008), Hammerschmidt et al. (2008), Sparling (2009), Frohne et al. (2012) and others. Apparent half-saturation value (K_m) of the model depends on the various encountered environmental conditions, with redox potential and OM lability as the governing factors.

Materials and methods

Unpublished data ($N = 602$) originated from sediment cores collected from Mediterranean environments, including near-shore environments (Pierre-Blanche lagoon and Toulon bay), continental shelf (Rhone pro-delta), canyon (Cap de Creus), abyssal plain (Algero-Provencal and Ionian basins), and Arctic Ocean margin and deep basins. Hg_T and MeHg determinations were performed according to Abi-Ghanem et al. (2011).

The gathered data ($N = 840$) used here originated from published works mentioned in Table 1. When figure data were not available, the DigiSoft program (available for free, download at http://gss.srce.hr/pithos/rest/omanovic@irb.hr/files/Software/) software was used to convert data points of the published graphs into numerals.

The Michaelis–Menten equation is frequently used to describe enzyme-catalyzed processes, as it relates to the metabolic conversion of a compound. The Michaelis–Menten fitting has successively described the methylation rate versus Hg^{II} concentration from experiments performed either on isolated bacteria

Table 1 Sources of published data used in the Michaelis–Menten model

Area	Reference
Lebanese coast	Abi-Ghanem et al. (2011)
Patuxent estuary	Benoit et al. (1998)
Rivers, lakes, wetlands and marine margins	Benoit et al. (2003)[a]
Karlshäll, Köpmanholmen and Skutskär estuaries	Drott et al. (2008)
Venice lagoon	Han et al. (2007), Guedron et al. (2012)
Long Island sound	Hammerschmidt and Fitzgerald (2004)
New England shelf	Hammerschmidt and Fitzgerald (2006)
Elbe river	Hintelmann and Wilken (1995)
Western Atlantic shelf and slope	Hollweg et al. (2010)
Kastela bay, Krka and Öre estuaries	Kwokal et al. (2002), Mikac et al. (2004)
Chesapeake bay	Mason and Lawrence (1999), Mason et al. (1999)
Seine estuary	Mikac et al. (1999)
Rupel, Deule, Seine and Soča rivers	Mikac et al. (2004)
Scheldt estuary	Muhaya et al. (1997)
Thau lagoon	Muresan et al. (2007)
Berre lagoon	Rigaud et al. (2013)
Passamaquoddy bay	Sunderland et al. (2006)

[a] Data compilation

strain (e.g. the *Desulfovibrio desulfuricans* LS isolated from salt marsh sediment, Choi et al. 1994), or directly on bulk sediments (e.g. King et al. 1999). Although normally used to model kinetic results (i.e. product formation rate versus substrate concentration), some authors also used such relationships between product and substrate concentrations. For instance, MeHg or Hg_T contents in fish tissues versus aqueous Hg_T were properly depicted using Michaelis–Menten curves by Brent and Kain (2011) and Mathews et al. (2013), respectively. Even empirical, such fits offer the advantage of a mechanistic foundation (i.e. enzymatic processes governing Hg methylation) and provide benchmarks for maximum methylation and half-saturation constant, parameters which can be confronted to laboratory or field experiments. Michaelis–Menten model was fit using SigmaPlot 10.0 software.

Results and discussion

The data couples spanned over six and five orders of magnitude for Hg_T and MeHg, respectively: from 3.1×10^{-3} to 1.1×10^{3} nmol g^{-1} and from 3.9×10^{-5} to 3.6×10^{-1} nmol g^{-1}, thus going from pristine to heavily contaminated sediments. Considering the entire data set, we achieved a highly significant ($R^2 = 0.70, N = 1{,}442, p < 0.001$) overall relationship with the following equation:

$$\mathrm{MeHg} = \frac{a \times \mathrm{Hg_T}}{K_m + \mathrm{Hg_T}},$$

where "a" is the saturation MeHg concentration (0.277 ± 0.011 nmol g^{-1}) and "K_m" estimates the H_{g_T} concentration, which corresponds to MeHg half-saturation (188 ± 15 nmol g^{-1}) (Fig. 1). As K_m increases, methylation efficiency decreases.

This Michaelis–Menten function corroborates that sediment MeHg concentrations are directly dependent of Hg_T concentration taken as a proxy of the methylation substrate (Hg^{II}), with an asymptotic MeHg concentration (a) mainly defined by data from Sweden riverine and estuarine sediments heavily contaminated by chlor-alkali activities (Drott et al. 2008). Such a saturation point was already noticed for contaminated sediments by Benoit et al. (2003). This maximum, theoretically due to Hg^{II} saturation of the methylation enzymatic systems, illustrates a more complex

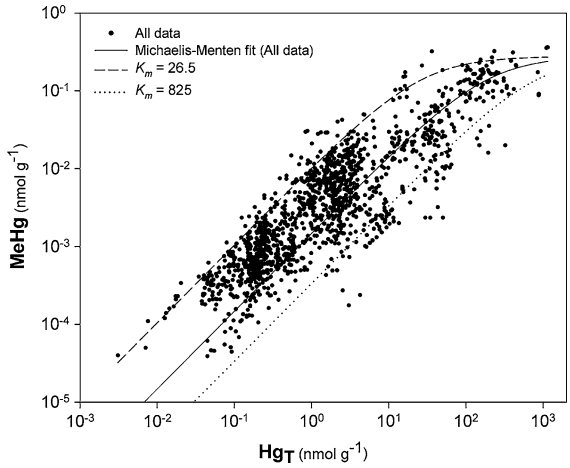

Fig. 1 Overall Michaelis–Menten type relationship ($p < 0.001$) between 1,442 couples of MeHg and Hg_T concentrations in aquatic sediments. MeHg/Hg_T couples from various aquatic sediments including marine abyssal, coastal, lagoonal, estuarine, lacustrine and riverine sediments ranging from pristine environments to heavily polluted ones, and from aerobic to sulfidic environments. The gathered data used here originate from published (Table 1) and present authors' unpublished works. When figure data were not available the DigiSoft program (available free for download at http://gss.srce.hr/pithos/rest/omanovic@irb.hr/files/Software/) software was used to convert data points of the published graphs into numerals

situation earlier qualified as "mercury accumulation paradox" (Schaefer et al. 2004). The Michaelis–Menten type relationship calculated here is the combination of multiple counteracting enzymatic reactions. As suggested by several authors (Marvin-Dipasquale and Oremland 1998; Marvin-Dipasquale et al. 2000; Segade et al. 2010), the asymptotic MeHg concentration can be interpreted as a modification of the reductive demethylation pathways in contaminated sediments, resulting from a methanogen to SRB demethylation shift when Hg^{II} or MeHg contents exceed a threshold value. Oxidative or reductive demethylation pathways would have indeed striking different consequences in the mercury cycling in the sediment. As quoted by Segade et al. (2010), the end-product of the reductive demethylation is gaseous Hg^0, a species which can escape from the sediment allowing its real detoxification, whereas the oxidative demethylation generates an Hg^{II} end-product which may be recycled in the methylation pathway.

The K_m value (188 ± 15 nmol g^{-1}) constitutes a relatively stable estimate, as the coefficient of variation falls below 8 %. However, keeping the

asymptotic a value of the equation fixed at 0.277 nmol g^{-1}, peculiar K_m values exhibit large variations (Table 2) depending on the environmental characteristics and sites, illustrated by the K_m increase when methylation efficiency decreases. Ranking the 1,442 Hg_T–MeHg couples according to their K_m values, it appears that (i) 5 % of Hg_T–MeHg couples are lower than 26.5, with 93 and 75 % of them are from surface sediments ($\leq$2 cm) and pristine sediment, respectively, and that (ii) 5 % highest K_m values are higher than 825, with 97 % of them correspond to deep (>10 cm) contaminated sediments. In addition, relatively low K_m values (139 ± 12 nmol g^{-1}) characterizes surface sediments ($\leq$2 cm) compared to that of sediments collected below 10 cm depth (223 ± 10 nmol g^{-1}, Table 2). Furthermore, the K_m values for the samples collected in open ocean are much lower than those for the river samples, whereas intermediate values characterized coastal and lagoonal samples (Table 2).

Interestingly, the Michaelis–Menten model can be simplified, for $Hg_T \ll K_m$, as a simple ratio: MeHg = $b \times Hg_T$ with $b = \frac{a}{K_m} \times 100$. The calculated b value is 0.15 % for our entire data set, and ranges from 0.03 to 1.05 % for the lowest and highest methylation efficiencies, respectively (see Supplementary information Fig. SI1). This is consistent with previous observations showing that MeHg/Hg_T ratios are a good proxy for net Hg methylation rates (e.g. Benoit et al. 2003; Hammerschmidt and Fitzgerald 2004, 2006; Guimarães et al. 2006; Drott et al. 2008). However, for the highest Hg_T values, the MeHg/Hg_T ratios notably decrease (Fig. SI2). This suggests that a "ratio model" does not fit the entire data set and, consequently, the diversity of the encountered environmental situations, as the Michaelis–Menten model does.

In summary, (i) sediments collected at depth >10 cm ($N = 228$) exhibit higher K_m than surface ones (0–2 cm), and (ii) freshwater and contaminated coastal sediments exhibit higher K_m than marine sediments. In other words, oxic/suboxic sediments and those originating from autochthonous marine settling material present higher net methylation rates

Table 2 K_m values for Michaelis–Menten type relationships between MeHg (nmol g^{-1}) and Hg_T (nmol g^{-1}) within various sediment types (values obtained keeping the asymptotic a parameter of the equation fixed at 0.277 nmol g^{-1})

Type of sediment	K_m	R^2 (n) p	Location	Hg_T level (nmol g^{-1})
Highest points (5 %)	14 ± 2	0.94 (72) < 0.0001	Surface sediment from various region (and heavily contaminated sediments)[a]	<1 (and >100)[a]
Lowest points (5 %)	1,870 ± 70	0.93 (72) < 0.0001	Toulon and Kastela bays, Venice and Berre lagoons, Elbe, Seine and Soča rivers and estuaries	10–1,000
Surface (<2 cm)	139 ± 12	0.41 (226) < 0.0001	All sites	<1–1,000
Deep (>10 cm)	223 ± 10	0.75 (550) < 0.0001	All sites	<1–1,000
Rivers	327 ± 38	0.38 (149)	Deule, Elbe, Rupel, Seine, Soča	>1
Estuaries	159 ± 20	0.64 (171) < 0.0001	Krka, Karlshäll, Köpmanholmen, Öre, Patuxent, Seine, Scheldt and Skutskär estuaries	>0.1
Lagoons	223 ± 16	0.10 (201) <0.10	Berre, Pierre-Blanche, Thau and Venice (Mediterranean lagoons)	0.1–10
Bays and shelves	168 ± 5	0.79 (642) < 0.0001	Chesapeake, Kastela, Passamaquoddy and Toulon bays, Lebanese coast, Rhone delta, Long Island Sound	<1–1,000
Open sea	89 ± 8	0.31 (277) < 0.0001	Abyssal plains and slope (Arctic Ocean, Mediterranean Sea, Atlantic Ocean)	<1
Abyssal plain	24.7 ± 0.2	0.99 (260) < 0.0001	Mediterranean Sea and Arctic Ocean	<0.5

[a] Data defining the asymptotic value of the equation, i.e. from Sweden riverine and estuarine sediments, heavily contaminated by chlor-alkali activities (Drott et al. 2008)

than anoxic and/or continental derived sediments. It also suggests that authigenic particles from the water column may be MeHg-enriched before being deposited and incorporated in surficial sediment, as earlier suggested by Muresan et al. (2007) for a lagoonal environment. Gilmour et al. (1998) and Benoit et al. (2003) already noticed that highest MeHg/Hg ratios were found in sediments where sulfate reduction was high but sulfide accumulation was low, such as sediments' upper layers and continental slopes. Han et al. (2010) also concluded from experiments with sulfate-limited sediments that Hg^{II} active methylation "possibly occurred by syntrophic processes arising between methanogens and sulfidogens". It has been recognized that in mildly reductive conditions, $HgS^0(aq)$, $Hg(SH)^0(aq)$ and uncharged mercury molecules such as Hg-cysteine complexes or even HgS particles facilitate mercury uptake in methylator microorganisms (Benoit et al. 1999; Drott et al. 2007; Schaefer and Morel 2009; Graham et al. 2012). Conversely, enhancement of dissolved sulfide in anoxic sediments may inhibit MeHg production (Benoit et al. 1999; Hammerschmidt et al. 2008). It is interesting to note that high K_m values for contaminated sediments are in agreement with the results of Drott et al. (2008) and Hines et al. (2000) showing that demethylation of MeHg progressively increases with depth in such sediments.

The differences between freshwater and marine sediments K_m values are likely to be interpreted in terms of OM reactivity since the organic carbon (OC) taken as a whole does not seem to be an overall explanatory factor for MeHg concentration. Indeed, from the 617 Hg_T–MeHg couples associated with OC contents, the significance of the MeHg versus OC relationship is not better than that of the Hg_T versus OC, and the $MeHg/Hg_T$ ratio appeared not to be related to OC (Fig. SI3A–C). It is generally observed that OM is more abundant in river and near-shore sediments than in open ocean sediments. However, it is also generally accepted that the continental OM accumulated in rivers and estuaries is more mature than the freshly deposited OM in the high productive area of the ocean margins (Arnost and Holmer 2003). This suggests that labile fresh OM present at the shelf margin is more effective in fuelling the microbial methylating activity than refractory OM, consistently with the hypothesis of Ravichandran (2004). To check the involvement of OM degradability in determining the relative MeHg abundance, we compared the $MeHg/Hg_T$ ratios with the amino acid concentrations available from the sediment of Cap de Creus canyon (Fig. 2). Considering nitrogenous compounds, especially amino acid, as the most hydrolysable OM present at the N.W. Mediterranean margin (Buscail and Germain 1997), it can be deduced from Fig. 2 that the OM lability is a limiting factor of the Hg methylation. This evidence agrees with an earlier study on MeHg distribution in harbour marine sediments which stated that allochthonous organic material attenuates gross and net rates of MeHg production (Hammerschmidt et al. 2008). Drott et al. (2008) likewise showed that differences in the primary production and subsequent availability of easily degradable OM (serving as electron donor for methylating bacteria) was indicated to be the most important factor behind the observed differences in $MeHg/Hg_T$ ratios and so K_m values among sites.

We conclude that, in sulfidic and non sulfidic pristine and heavily polluted sediments from both freshwater and marine environments, the abundance of MeHg relative to Hg_T depens on Hg availability and OM reactivity. Oxic and suboxic sediments receiving both fresh OM and high Hg deposition, such as oceanic margins, favor MeHg accumulation. Only a part of MeHg is preserved in deep anoxic sediments leading to low $MeHg/Hg_T$ ratios. We can speculate furthermore that a Michaelis–Menten type model linking MeHg to inorganic Hg^{II} could also be valid for the oceanic water column.

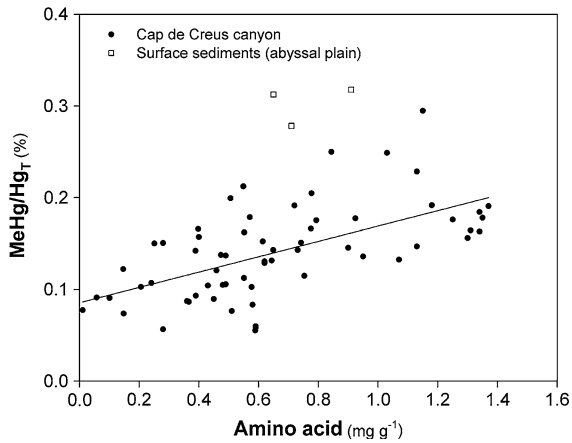

Fig. 2 Relationship ($p < 0.001$) between $MeHg/Hg_T$ ratios and amino acid (proxy of labile organic matter) in the sediment of the Cap de Creus canyon (NW Mediterranean)

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