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Adsorption of aqueous inorganic mercury and methylmercury on suspended kaolin: influence of sodium chloride, fulvic acid and particle content

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The main tendencies in the adsorption of dissolved inorganic mercury (Hg^{2+}) and methylmercury ($MeHg^{+}$) on suspended kaolin particles have been investigated in synthetic aqueous solutions. The influence of NaCl, fulvic acid (FA) and suspended particulate matter (SPM) in the system has been studied at a constant pH of 7.2. The experiments were arranged according to a full factorial design with three factors (NaCl, FA SPM) at low (−) and high (+) levels. A central point (0) was repeated four times to estimate the reproducibility of the results. The low and high levels investigated were 0–35 g l^{-1}, 0–10 mg l^{-1} and 0.5–5 g l^{-1} for the concentrations of NaCl, FA and kaolin respectively. In order to match the linear range of the analytical technique the total concentration of mercury (as Hg^{2+} or $MeHg^{+}$) in the synthetic suspensions was 25 ng ml^{-1}. After chemical stabilization of each suspension, the Hg^{2+} or $MeHg^{+}$ content in the clear filtrate was determined by an automated hyphenated technique combining the following steps: (i) derivatization by hydride generation, (ii) preconcentration by cryogenic trapping, (iii) separation by packed column gas chromatography and (iv) detection by quartz furnace atomic absorption spectrometry. The removal of Hg^{2+} and $MeHg^{+}$ from the solution *via* adsorption on particles ranged, respectively, from 12.4 to 94.9% and from 1.7 to 45.6% of the total mercury compound concentration. High concentrations of NaCl led to lower adsorption rates of both mercury species. The adsorption of $MeHg^{+}$ was enhanced in the presence of FA, whereas that of Hg^{2+} was clearly diminished. High levels of SPM promoted the adsorption of both Hg^{2+} and $MeHg^{+}$ on kaolin particles. Several experiments were also conducted to check the adsorption rate of Hg^{2+} and $MeHg^{+}$ on natural particles collected in the Gironde estuary. The results confirmed the general trends observed when using reference kaolin particles. The results presented here will be helpful for groups modelling the physico-chemical behaviour of mercury in estuary conditions.

Keywords: mercury; methylmercury; adsorption; kaolin; clay; distribution; hydride generation; ethylation

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INTRODUCTION

The study of the biogeochemical cycle of mercury in estuarine environments has been a field of continuous interest during the last decades. Estuarine sediments are believed to be an important sink of mercury.[1] Under favourable physico-chemical conditions, inorganic mercury (Hg^{2+}) in surface sediments is transformed into methylmercury ($MeHg^{+}$) through biotic or abiotic processes.[2,3] Mercury in sediments is therefore likely to be re-

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mobilized into the water layer in a more toxic form. It has been demonstrated that $MeHg^+$ is able to accumulate in fish tissue and enter the human trophic chain in this way.[4–6] The distribution of Hg^{2+} and $MeHg^+$ between the dissolved and particulate phases in estuarine environments is consequently of outstanding importance. Particulate mercury is expected to join the top sediments in the mouth of the estuary and undergo methylation processes, whereas dissolved mercury will more probably be expelled to the sea.

In estuarine aqueous environments mercury is believed to be mostly associated with suspended particulate matter (SPM).[7] Organics, salinity, the amount and nature of particles and pH seem to play an important role in the adsorptive behaviour of mercury species on suspended particles.[8] Humic and fulvic substances have been reported to form very strong complexes with mercury species.[9–11] Organic coatings lead consequently to enhanced sorption of Hg^{2+} and $MeHg^+$ on particles of different origin, such as iron and manganese oxides, clay material, silica and natural sediments.[12] However, to date, reports systematic investigations of the adsorptive properties of mercury species on different surfaces under different conditions are rare. Gagnon and Fisher[12] investigated the adsorptive properties of both Hg^{2+} and $MeHg^+$ on particles of different nature in seawater. The distribution coefficients K_d obtained greatly differ from one surface to another, probably due to differences in the nature and amount of binding sites. The K_d values of Hg^{2+} and $MeHg^+$ are comparable, but usually slightly lower for $MeHg^+$. Gunneriusson *et al.*[13] obtained similar conclusions when investigating the adsorption of Hg^{2+} and $MeHg^+$ on hydrous goethite in synthetic solutions at different pH and constant ionic strength. On average, about 80% and 15% of Hg^{2+} and $MeHg^+$ was respectively adsorbed on hydrous goethite. These observations have been partially confirmed in recent studies performed directly in several European[7,14–16] and American[17] estuaries.

The objectives of this study are (i) to draw a first picture on the adsorption behaviour of Hg^{2+} and $MeHg^+$ on kaolin particles in synthetic aqueous solutions at constant pH and (ii) to establish the statistical significance (or non-significance) of sodium chloride (NaCl), fulvic acid (FA) and particle content and their combinations on the adsorption rate of those mercury species. The influence of the variables will be further investigated in the future in the light of the results obtained here. Extrapolation of the results may be useful in the interpretation of the physico-chemical behaviour of mercury in estuarine environments.

EXPERIMENTAL

Reagents and materials

All chemicals used were of analytical-reagent grade (Merck, Germany) unless otherwise stated. Milli-Q quality water (Millipore, USA) was used throughout. NaCl was dissolved in water to obtain a 140 g l^{-1} stock solution. An FA stock solution (20 mg l^{-1}) was prepared by dissolving dry FA (Langford Fulvic Acids, Canada) in acidified water (pH 2, HCl Suprapure) and filtering at 0.45 μm prior to use. Natural kaolin (KGa-1, Washington County, Georgia, USA), with a certified specific surface of 8.2 m^2 g^{-1}, was obtained from the Clay Mineral Society (USA). Particle matter collected in the Gironde estuary during a sampling campaign in June 1997 was also used in several experiments. These particles were sampled in fluid mud accumulated in bottom water and stored in the dark at −30 °C until their conditioning. After defrosting over 48 h at 4 °C, and in order to remove the coated organic matter and dissolve manganese and iron oxides, the particles were suspended in glacial acetic acid (Fluka, $\geq$99.7%) and treated in on ultrasonic bath for 30 min. The suspension was centrifuged, washed three times with water and dried at 60 °C in an oven for 30 h.

Mercury chloride and methylmercury chloride were purchased from Strem Chemicals (USA) and used without further purification. Stock solutions of 1000 mg l^{-1} $MeHg^+$ and 2000 mg l^{-1} Hg^{2+} were prepared in methanol and 1% HNO_3 respectively. Appropriate dilutions of the stock solutions were made in water. Both stock and working standard solutions were stored in darkness at 4 °C and were shown to be stable over several weeks. The pH of the synthetic solutions was adjusted to 7.2 by addition of 5 g l^{-1} of phosphate buffer solution. Acidification of the filtrates was carried out by addition of concentrated HCl solution (Merck, Suprapure). Traces of Hg^{2+} were removed from the commercial HCl solution by sub-boiling distillation using a set-up similar to that described by Mattison.[18] 4% $NaBH_4$ (Fluka, Germany) aqueous solutions were prepared immediately before use and kept in ice during the analysis procedure. Helium (99.995%, L'Air Liquide, France) was used as carrier gas and the chromatographic column was packed with Chromosorb W-HP (60–80 mesh size) coated with 10% SP-2100 supplied by Supelco (USA) and silanized with hexamethyldisilazane (Prolabo, France) prior to use.

The synthetic suspensions were prepared in 22 ml Pyrex vials with Teflon caps supplied by Supelco and shaken using an automatic shaker (Ika Labortechnik, KS 250). The solutions were filtered through 0.45 µm pore-size polycarbonate filters (diameter 47 mm) purchased from Millipore. Prior to use, the filters were soaked in 1% HNO_3 solution for several days and subsequently rinsed with Milli-Q water.

All the glassware used for dilution and storage was cleaned with RBS 50 detergent, thoroughly rinsed with tap water, soaked overnight in a 10% HNO_3 solution and finally rinsed with Milli-Q water before use.

Instrumentation

The concentration of Hg^{2+} or $MeHg^+$ in the filtered solutions was determined by an automated on-line hyphenated system developed for metal and metalloid speciation analysis, which combines derivatization of the sample by hydride generation (HG) or ethylation (Eth), preconcentration by cryofocusing (CT), separation by packed column gas chromatography (GC) and detection of the target analytes by quartz furnace atomic absorption spectrometry (QFAAS). A full description of the system can be found elsewhere.[19]

Experimental procedure

The influence of the concentration of NaCl, FA and SPM on the adsorption of Hg^{2+} and $MeHg^+$ on kaolin was investigated using synthetic solutions prepared in the laboratory. The experiments were arranged according to a two-level full factorial design with three factors, i.e. NaCl, FA and SPM (A, B, C), at high (+) and low (−) levels. A central point (0) was replicated four times to estimate the residual variance and to check for non-linear trends in the response. This experimental design provides full information with a low number of observations.[20] It allows for the accounting of possible synergistic effects among factors. In addition, statistically significant effects can be differentiated from non-significant ones by the analysis of variance (ANOVA) of the results.

The low, central and high levels of the factors are shown in Table 1. The combinations (tc) of the factorial design are shown in the Yates order[20] in the first four columns of Table 2. The first eight tc points in Table 2 consider all the possible combinations among factors at high and low levels; the final four points correspond to the replicates of the central point. The factorial design shown in Table 2 was blocked to obtain three groups of four experiments each, in such a way that at least one central point was included in each group. The solutions corresponding to each group were prepared and analysed in random order to avoid systematic errors. Each block of experiments was processed on different and consecutive days. One set of 12 experiments was processed separately for each mercury species.

For each tc, the appropriate amount of kaolin was placed in a 22 ml pre-weighed Pyrex vial. 0, 2.5 or 5 ml of 140 g l^{-1} NaCl and 0, 5 or 10 ml of 20 mg l^{-1} FA solutions were successively added to the vials, and the volumes of the suspensions were increased to 20 ml with water. 200 µl of 5 g l^{-1} phosphate

Table 1 Levels of the factors in the two-level full factorial design

Factor	Level (+)	Level (0)	Level (−)	Units
NaCl (A)	35	17.5	0	g l^{-1}
FA (B)	10	5	0	mg l^{-1}
SPM (C)	5	2.5	0.5	g l^{-1}

Table 2 Observations (tc) of the factorial design in the Yates order and percentages of mercury species removed from the solution in each case. $RSD_{(000)}$ (%): relative SD of the four replicates of the central point

				Removal (%)	
tc	A	B	C	Hg^{2+}	$MeHg^+$
(1)	−	−	−	84.4	12.0
a	+	−	−	26.0	1.7
b	−	+	−	54.4	26.0
ab	+	+	−	12.4	6.0
c	−	−	+	94.9	33.8
ac	+	−	+	43.2	18.0
bc	−	+	+	58.0	45.6
abc	+	+	+	33.6	33.6
$Zero_1$	0	0	0	16.4	10.4
$Zero_2$	0	0	0	19.2	12.2
$Zero_3$	0	0	0	16.8	14.0
$Zero_4$	0	0	0	18.8	14.4
$RSD_{(000)}$ (%)				7.89	14.4

Table 3 Observations (tc) prepared using the particles collected in the Gironde estuary instead of kaolin, together with the percentages of mercury species removed from the solution in each case

tc	A	B	C	Removal (%) Hg^{2+}	Removal (%) $MeHg^{+}$
(1)	−	−	−	90.0	58.4
a	+	−	−	20.4	17.2
c	−	−	+	94.0	64.4
ac	+	−	+	75.2	14.8

buffer was added to keep the pH of the suspension at 7.2 throughout the adsorption procedure. After shaking the resulting suspensions for 6 h, 500 ng of Hg^{2+} or $MeHg^{+}$ was added and the suspensions were again shaken for 6 h. Longer stabilization times did not result in higher removal of mercury species. The equilibrated suspension was then filtered through a 0.45 μm poresize polycarbonate filter. Small sample volumes (20 ml) prevented clogging of the filters. The clear filtrate was collected directly in a 22 ml Pyrex vial, acidified with 50 μl of concentrated HCl and stored in darkness at 4 °C until analysis. Preliminary assays confirmed that no adsorption of either of the dissolved mercury species was occurring on the filter membrane during the filtration procedure, and that acidification of the filtrate with HCl leads to a negligible loss of mercury species via adsorption on the wall.

The concentration of Hg^{2+} or $MeHg^{+}$ in the filtrates was determined in an electrically heated quartz furnace by atomic absorption spectroscopy after derivatization of the sample by HG and preconcentration of the generated volatile mercury species by cryogenic trapping. HG is now a well established method for mercury speciation, provided that correct working conditions are observed.[21–24] The optimization of the method provides quantitative conversion of the target analytes (Hg^{2+} to Hg^{0} and $MeHg^{+}$ to MeHgH) and the new species formed have been proved to be stable.[23–25] The optimal conditions for the analysis of aqueous samples are described elsewhere.[19] In order to minimize interferences due to matrix effects, the amount of Hg^{2+} or $MeHg^{+}$ in each filtrate was determined by a six-point standard addition method. Blanks were run after every three analyses to check for possible memory effects. Analyses of standard solutions with 5 ng of Hg^{2+} or $MeHg^{+}$ were performed periodically to check the overall sensibility of the analytical set-up.

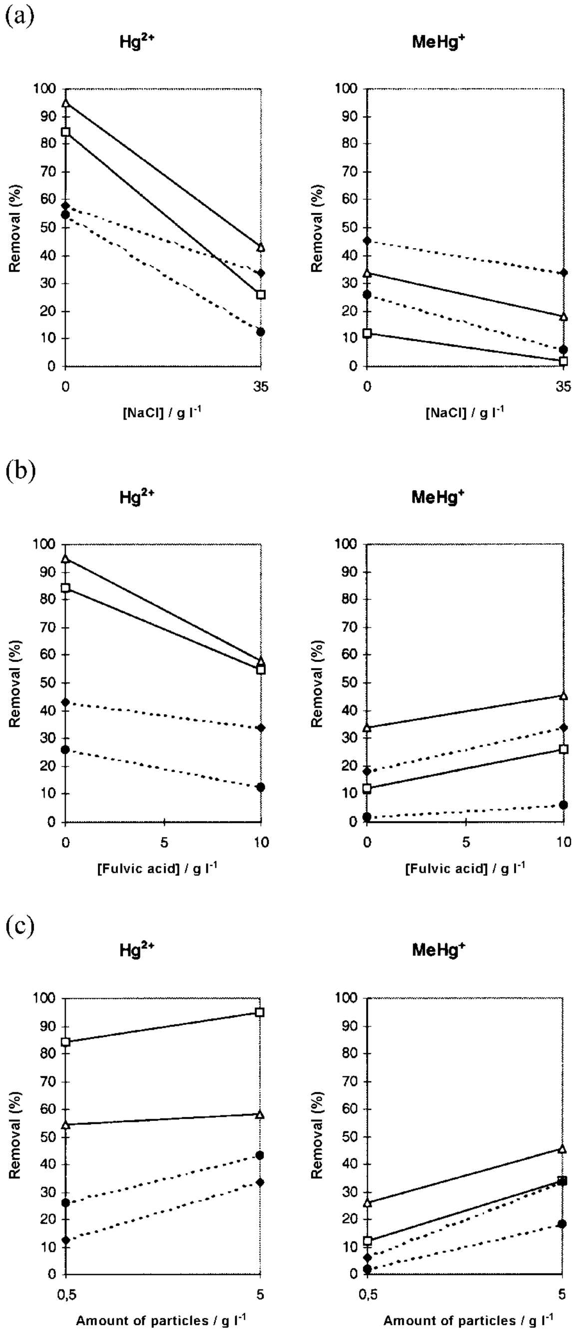

Figure 1 Influence of NaCl, FA and SPM on the adsorption of Hg^{2+} and $MeHg^{+}$ on kaolin particles: (a) influence of the NaCl concentration (●, +FA, −SPM; △, −FA, +SPM; ◆, +FA, +SPM; □, −FA, −SPM); (b) influence of the FA concentration (●, +NaCl, −SPM; △, −NaCl, +SPM; ◆, +NaCl, +SPM; □, −NaCl, −SPM); (c) influence of the amount of SPM (●, +NaCl, −FA; △, −NaCl, +FA; ◆, +NaCl, +FA; □, −NaCl, −FA).

Several experiments were also performed using natural particles collected in the Gironde estuary instead of the reference kaolin. The identifications and compositions of the synthetic solutions prepared using the particles from the Gironde are shown in the first four columns of Table 3. The high (+) and low (−) levels are the same as those in Table 1. Each synthetic solution was prepared and analysed following the same procedure described above. Again, one set of four experiments was processed for each mercury species.

RESULTS

The results obtained after the analysis of the filtrates are provided in the last two columns of Table 2. They are expressed as percent of Hg^{2+} or $MeHg^{+}$ removed from the aqueous phase after the stabilisation and filtration of the suspensions prepared as described in the Experimental section. Preliminary work confirmed that the loss of dissolved mercury species via adsorption on the filter membrane and vial walls is negligible. Consequently, we assume that the percentage of mercury species removed corresponds to the part associated to the particulate phase that has been retained by the filter (<0.45 μm fraction). The low standard deviations (SDs) obtained in the repetition of the central point show that a good reproducibility would be expected from the results. The effect of each factor (NaCl concentration, FA concentration and amount of kaolin) individually considered on the adsorption of the mercury species on kaolin particles is illustrated graphically in Fig. 1a–c. Lines between points in Fig. 1 represent trends, not necessarily linear responses. Qualitatively, the most outstanding features of the Hg^{2+} and $MeHg^{+}$ adsorption behaviour on kaolin particles may be summarized as follows: (i) on average, the adsorption of Hg^{2+} is more efficient than that of $MeHg^{+}$; (ii) increasing the saline content of the solution results in lower adsorption rates for both Hg^{2+} and $MeHg^{+}$; (iii) high amounts of kaolin promote the adsorption of both Hg^{2+} and $MeHg^{+}$; (iv) the presence of FA in the solution enhances the adsorption of $MeHg^{+}$ but inhibits that of Hg^{2+}.

From the statistical point of view, the slopes in Fig. 1 differ significantly from zero (i.e. the influence of the variable represented on the *x* axis is statistically significant) if the difference between the corresponding high and low values is higher than the SD of the central point ($RSD_{(000)}$).[20] In order to check in a quantitative way the statistical significance of each factor or combination of factors on the adsorption behaviour of Hg^{2+} and $MeHg^{+}$, ANOVA of the results was performed. The results arising from ANOVA are summarized in Table 4. The influence of each factor or combination of factors (first column in Table 4) on the adsorption of Hg^{2+} and $MeHg^{+}$ is expressed in relative terms by the *average effect* (second and third columns in Table 4) estimated in the ANOVA calculation. A positive *average effect* means that the corresponding factor or combination of factors enhances the adsorption of the mercury species. The calculated values of the *F* statistics are also provided in the fourth and fifth columns of Table 4. The *F* test of comparison of variances checks the statistical significance of the factors and combinations among them on the response. The good reproducibility obtained in the analysis, together with the high influence of the factors on the adsorptive properties of the mercury species, has led to quite high values of *F*. *F* values higher than the critical one ($F_{crit} = 7.71$) indicate that the effect of the corresponding factor or combination of factors on the adsorption of the mercury species is statistically significant at the 95% confidence level. Significant factors are given in bold in Table 4. The effects of the three factors individually considered are significant for both mercury species. In addition, the combination between NaCl and FA and between NaCl and kaolin significantly enhance the adsorption of Hg^{2+} on kaolin particles.

Four suspensions were also prepared using the particles collected in the Gironde instead of kaolin. The compositions of these suspensions are shown in Table 3. The low and high levels are those appearing in Table 1. These suspensions were also processed as described in the Experimental section. The results obtained are collected in the last two columns of Table 3 and they are compared graphically with the results obtained when using kaolin in Fig. 2. The adsorption of both Hg^{2+} and $MeHg^{+}$ seems to be systematically higher on natural particles than on kaolin. The influence of the factors investigated on the adsorptive properties of the species, however, do not differ too much from the trends observed in the experiments with kaolin.

DISCUSSION

In our experiments, particulate mercury may arise from (i) direct adsorption of mercury species (Hg) on suspended particles (SP), (ii) aggregation of organic matter (FA) to suspended particles and subsequent adsorption of mercury species on the newly formed coated particle or (iii) association of mercury species with organic matter prior to adsorption of the organic complex on the suspended particle. Flocculation of colloids into bigger particles, which takes along trace mercury in the transformation from dissolved ('filter-passing', <0.45 μm) to particulate ('filter-retained', >0.45 μm) 'phase' is also possible. All these potential pathways will now be taken into consideration according to the results obtained on the influence of NaCl, FA and SP contents and their respective statistical significances.

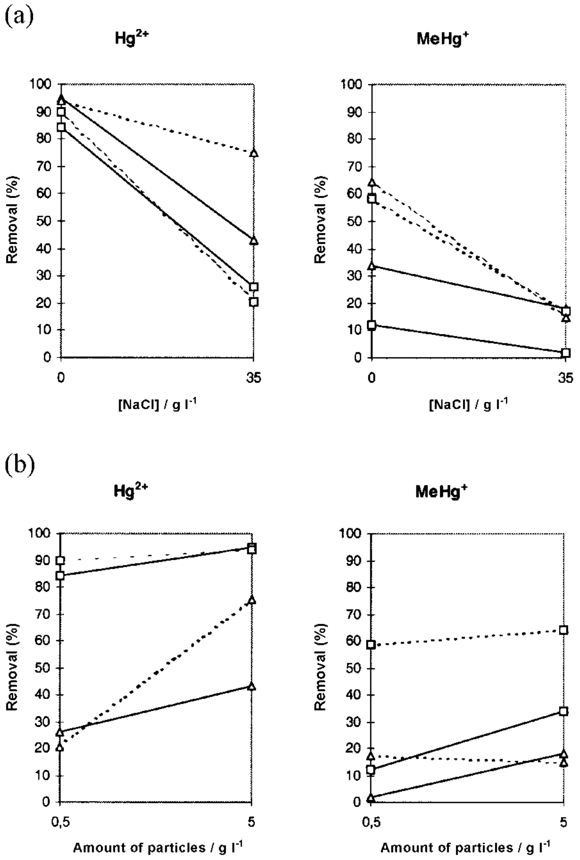

Figure 2 Influence of NaCl and SPM on the adsorption of Hg^{2+} and $MeHg^{+}$ on natural particles collected in the Gironde estuary (dashed lines). Comparison with the results obtained using kaolin particles (full lines): (a) influence of the NaCl concentration (□, −FA, −SPM; △, −FA, +SPM); (b) influence of the amount of SPM (□, −NaCl, −FA; △, +NaCl, −FA).

Effect of the ionic strength

Changes in ionic strength have been simply modelled by varying NaCl concentration. High NaCl content provides (i) Na^{+} cations, which effectively compete with mercury species for the anionic binding sites of kaolin, and (ii) Cl^{-} anions, which promote the formation of very stable and negatively charged chloro-complexes of mercury, especially $HgCl_4{}^{2-}$,[9] and MeHgCl.[26] Both facts facilitate desorption of mercury species from the suspended particles. In our experiments, increasing the concentration of NaCl leads to significantly lower removals in all the situations checked. The tendency is more pronounced in the case of Hg^{2+}, which results in the highest F value (i.e. statistical significance) found in this study. At high values of NaCl concentration, the extremely high stability of chloro-complexes of both Hg^{2+} and $MeHg^{+}$ tends to keep mercury predominantly in solution, masking any potential effect of FA aggregation onto

Table 4 Results from the ANOVA of the removals of Hg^{2+} and $MeHg^{+}$ from the solution, showing the statistical significance of the individual factors and the combinations of factors. Values in bold indicate significance at the 95% confidence level ($F_{crit} = 7.71$)

Factor or combination of factors	Average effect		*F* value	
	Hg^{2+}	$MeHg^{+}$	Hg^{2+}	$MeHg^{+}$
a	−22.1	−7.3	**1980**	**125**
b	−11.3	5.7	**515**	**77**
ab	5.5	−0.7	**121**	1.29
c	6.6	10.7	**175**	**270**
ac	3.0	0.3	**37.5**	0.23
bc	−0.4	1.1	0.53	3.07
abc	1.4	1.7	7.54	6.76

kaolin surfaces. The negative charge of the main complex, $HgCl_4^{2-}$, also makes unlikely the adsorption of Hg^{2+} on particles. Competition of Na^+ cations with the mercury species under investigation for the binding sites of the kaolin could also be partially responsible for this behaviour.

Effect of organic matter

FA is a good complexing agent for cationic mercury species such as Hg^{2+} and $MeHg^+$.[11] At the same time, it has been reported that the presence of FA enhances the adsorptive properties of clay.[12] At pH 7.2 the anionic form of the acid is predominant and ready to bond dissolved mercury, and will promote either solubility enhancement or organic phase aggregation of the mercury species. A decrease in the removal of Hg^{2+} with increasing FA content is observed for all the situations tested. $MeHg^+$ exhibits the opposite behaviour. Both effects are significant at the 95% confidence level. This behaviour suggests that Hg^{2+} forms very stable and soluble complexes with FA. On the other hand, the adsorption of $MeHg^+$ on kaolin is effectively enhanced by FA. Again, high salinity promotes formation of stable chloro-complexes, and the presence of FA allows the formation of soluble organic complexes and reduces the amount of non-coated particles of kaolin. In this case, both features are acting in same direction to lower the adsorptive removal of Hg^{2+}. This synergistic effect explains the statistically significant interaction found between NaCl and FA for Hg^{2+} ($F = 121$).

Effect of SPM

Kaolin is a ubiquitous and representative clay in natural waters and provides negatively charged binding sites at pH above 5.5, available for any cationic species.[8] The results obtained confirm the importance of the amount of suspended clay particles on the adsorption rate of the investigated mercury species on kaolin. Higher removals are systematically obtained for both Hg^{2+} and $MeHg^+$ when the content of kaolin is set at a high level. The effect is statistically significant in both cases. Solutions modelling marine salinity with the lower suspended matter content display the lowest Hg^{2+} removals, due to synergistic effects of increasing NaCl (i.e. stronger anionic chloro-complexes and competition for binding sites by Na^+ cations) content and decreasing suspended matter (i.e. less binding sites available). The interaction between NaCl and kaolin is also confirmed by the statistical significance obtained for Hg^{2+} at the 95% confidence level.

Kaolin versus particulate matter collected in the Gironde estuary

The experiments performed on real clay confirm the higher adsorptive properties of Hg^{2+} compared with those of $MeHg^+$. The general trends are qualitatively the same working with kaolin or natural sediment particles: (i) increasing NaCl results in lower removal by adsorption for both Hg^{2+} and $MeHg^+$ and (ii) higher suspended matter content appreciably increases the percentages removed from the aqueous phase, especially in the case of Hg^{2+}. Quantitatively, the removal of Hg^{2+} after filtration is comparable to that observed using kaolin, except when the high level of both NaCl and suspended matter is tested. In this case the removal is unexpectedly high, perhaps due to a larger amount of available sites on the surface of natural sediment particles or to a non-quantitative removal of manganese and iron oxides during the conditioning process of the particles with acetic acid. For $MeHg^+$, the percentage removed from the aqueous phase is, in general, higher with natural particles than using kaolin. Only at high levels of both NaCl and suspended matter is the removal not as significant as the general trend suggests.

Environmental implications

Removals of Hg^{2+} range from 12 to 94%, whereas those of $MeHg^+$ are markedly lower, ranging from 1.7 to 45.6%. The formation of very stable and negatively charged chloro-complexes is probably responsible for the low adsorption of both Hg^{2+} and $MeHg^+$ found at high salinities. $MeHg^+$ seems to adsorb more easily on kaolin particles coated with FA, whereas direct adsorption on uncoated kaolin is the preferred mechanism in the case of Hg^{2+}. Maintenance of Hg^{2+} in the aqueous phase may be favoured by the formation of very stable chelates between the FA and the divalent form of the metal. Finally, the increase of available binding sites for the mercury species when increasing the amount of kaolin is the logical reason for the higher removal found for both species in this situation.

The results obtained here do not allow us to draw a complete picture of mercury cycling in estuarine environments. Phenomena such as colloid-uptake and coagulation, thiol-group complexation in sediments under oxic/anoxic conditions or biological uptake and release all play an important role in the fate of mercury. Mercury cycling differs from one system to another, and very much depends on parameters that change with seasonal variations. However, some general trends may be derived from the results obtained here: (i) Hg^{2+} is more tightly associated with solid particulate matter than is $MeHg^+$; (ii) the fraction of mercury adsorbed is higher within the high turbidity zone present in most macrotidal estuaries;[16,27] (iii) high FA (i.e. humic substances) content promotes $MeHg^+$ adsorption but limits that of Hg^{2+}; (iv) although formation of strong and anionic chloro-complexes of both Hg^{2+} and $MeHg^+$ in seawater favours desorption from solid particles, a high percentage of mainly Hg^{2+} may still join the top sediments in the lower estuary after flocculation of suspended matter due to increasing salinity.

CONCLUSIONS

Suspended particles in estuaries act as a kind of buffer of metal concentration in water. At higher metal concentrations, due to remobilization/dissolution from sediments and soils, adsorption onto particles is favoured, whereas low metal concentrations result in improved desorption rates. A thorough knowledge of the adsorption/desorption rates and mechanisms under different conditions is, in consequence, mandatory when trying to model the physico-chemical behaviour of metals, and specifically mercury, in estuarine environments. The results presented here go in that direction and, even if they are partial and much work is yet to be done in this field, we believe that the information provided may help to draw a more exact picture of the mercury cycle in estuaries.

Only three of the factors that might affect the adsorption of mercury on specific clay particles of kaolin have been taken into account. The effect of other variables, such as pH, nature of particles, ionic strength or organic coatings, should also be investigated thoroughly. In addition, the concentration of both the metallic species and the variables considered here are slightly higher than those found in most of estuaries. The results, however, are expected to be able to be extrapolated to natural conditions. In fact, even though FA and kaolin cannot be regarded as representative of the different kinds of organic and suspended matter that can be found in different estuaries, the results obtained with natural particles collected in the Gironde estuary suggest that the adsorptive trends of mercury in such natural systems may not vary very much from those proposed here. Moreover, recent results obtained in the high turbidity zone of the Gironde estuary, characterized by a strong suspended clay particles load including manganese and iron oxides,[27] confirm that similar processes are occurring in the water column.

Finally, it is worthwhile pointing out that factorial design of experiments is established as a valid tool for studying the adsorptive properties of metals under estuarine conditions. The effect of important parameters such as salinity, FA and suspended clay particles, as well as their mutual interactions, on the adsorption/desorption processes occurring in estuaries can be investigated effectively. Moreover, the statistical significance of the parameters can be assessed using ANOVA of the results obtained.

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