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# Adsorption of mercury species on river sediments – effects of selected abiotic parameters

**Reserch Article**

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**Abstract:** Abiotic parameters (pH, temperature, current velocity, mercury species concentration, and sediment and aqueous media composition) influence mercury species ($MeHg^+$, $EtHg^+$, $PhHg^+$ and inorganic $Hg^{2+}$) adsorption on river sediments. The highest amount of adsorbed $MeHg^+$ and $EtHg^+$ (82-93% and 85-91% for static and agitated system, respectively) occurred at pH 3-4. For $PhHg^+$ the maximum adsorption (90% and 95% for static and agitated systems) was located over the broad 3-10 pH range, while for $Hg^{2+}$ (94% and 97% for static and agitated systems) it was at pH $\sim$ 3. Temperature (4.5-60°C) influenced the adsorption rate but not the quantity. Both rate and quantity increased in the order: static $<$ agitated $\leq$ stirred systems. The aqueous medium composition affected both rate and quantity. Sulfate caused the largest adsorption decrease for organomercury species (15-25% decrease); sulfide reduced $Hg^{2+}$ adsorption about 67%. Cations at pH 5.2 reduced either the adsorption rate ($Ca^{2+}$, $Al^{3+}$) or the total adsorption ($Zn^{2+}$, $Fe^{3+}$). Positive correlations were found between sediment C, N, S content as well as cation exchange capacity (CEC) with mercury adsorption ($R =$ 0.45-0.66, 0.56-0.89, 0.45-0.61 and 0.55-0.73, respectively) while negative correlations were observed with Fe and Al ($R =$ -0.63 to -0.90 and -0.65 to -0.86, respectively).

**Keywords:** *Mercury species • Adsorption • River sediments*

## 1. Introduction

Natural bio-geochemical cycles describe the transport, behavior and fate of mercury in the environment. They are characterized by evaporation of the element from soil and surface waters, followed by atmospheric transport, deposition back to land and surface waters and sorption by soil or sediment. Particulate-bound mercury can be converted to insoluble mercury sulfide or bio-converted into more volatile or soluble forms that re-enter the atmosphere or bioaccumulate [1,2]. The cycle is complicated by numerous mercury species (*e.g.* $Hg^0$, $Hg^{2+}$, $Hg_2^{2+}$ and organomercury species $RHg^+$, $R_2Hg$) present.

Sediments play a major role in the dynamics of natural aquatic systems. The mobility and fate of mercury depends largely on sediment mineralogy and surface chemistry as well as the water environment [3]. Better understanding of adsorption/desorption processes and rates is necessary to assess and predict pollution [4]. Partition among dissolved and particulate phases is the outcome of competition among ligands in solution (truly dissolved), colloidal particles, and organic and inorganic materials. $Hg^{2+}$, $MeHg^+$ and 2-methoxyethylmercury adsorption and desorption kinetics on soils and sediments have been investigated [4-9]. It was assumed that three concurrent reactions, *i.e.*, one rapid and reversible, another slow and reversible, and an irreversible reaction

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affected adsorption/desorption, since three different kinds of reactive sites are present on soil or sediment [5,9].

Organic matter, salinity, the amount and nature of particles and pH seem to play important roles in the adsorptive behavior of inorganic mercury ($Hg^{2+}$) and methylmercury on sediment [10-12]. Humic and fulvic substances, which form very strong complexes with mercury species, also influence their adsorption [13]. However, reports describing mercury adsorption under different conditions vary. Little information on the adsorption/desorption of phenyl- or ethylmercury on sediment is available.

The influences of selected abiotic parameters (sediment/aqueous phase ratio, mercury concentration, pH, temperature, movement of the sediment/water mixture in the bioreactor, and sediment and aqueous phase compositions) on the adsorption of mercury species ($MeHg^+$, $EtHg^+$, $PhHg^+$ and $Hg^{2+}$) by river sediment were investigated. Both the rates and quantities of mercury species adsorption as well as their differences were examined. Bacterial transformations of mercury in the systems examined were negligible.

# 2. Materials and methods

## 2.1. Chemical and reagents

Inorganic mercury calibration standard (1.000±0.002 g $L^{-1}$ $Hg^{2+}$ in 2% v/v $HNO_3$) was obtained from the Czech Metrological Institute (Prague, Czech Republic). Methylmercury chloride ($MeHg^+$) and phenylmercury chloride ($PhHg^+$) were purchased from Sigma-Aldrich. Ethylmercury chloride ($EtHg^+$) was purchased from Supelco (Munich, Germany). Stock standard solutions of $MeHg^+$, $EtHg^+$ and $PhHg^+$ (c = 1 g $L^{-1}$ ) were prepared in methanol. Working standards (20 and 50 µg $L^{-1}$ ) were prepared from the stock solutions by diluting with deionized water (AquaDem-02, AquaOsmotic, Tišnov, Czech Republic) further purified in a Millipore Milli-Q system (Bedford, MA, USA). The resistivity was greater than 16 MΩ cm. Analytical grade HCl, $HNO_3$, NaOH, NaCl, $Na_2SO_4$, $Na_2S$, $FeCl_3$, $Fe_2(SO_4)_3$, $MnSO_4$, $MnCl_2$, $AlCl_3$, $ZnCl_2$, $Na_3PO_4$, urea, thiourea, L-cysteine were purchased from Penta (Chrudim, Czech Republic). All glassware was borosilicate glass. It was soaked overnight in 10% $HNO_3$ and rinsed with DI water just before use. Hydrochloric acid, nitric acid and sodium hydroxide were used to adjust the pH.

## 2.2. Sediment samples

Sediment samples were collected from four Moravian rivers during October 2007. The GPS positions and dates are given in Table 1. Surface samples were taken (maximum depth 15 cm), placed in plastic bottles, stored in coolers, and transported to the laboratory. They were lyophilized under vacuum at –51 ± 1°C for 48 h. Sediment aggregates were manually crushed in a borosilicate mortar and sieved through a 2 mm high density polypropylene (HDPP) screen. All experiments were conducted using the <2 mm sediment fraction.

## 2.3. Adsorption of mercury species on sediments

Sediment samples (20 ± 0.01 g DM) were weighed into 500 mL brown screw-cap glass bottles and 250 mL of 20 or 50 µg $L^{-1}$ mercury species working standard was added. Samples were shaken using an orbital shaker (BioSan, Riga, Latvia) at 180 rpm and 10 mm amplitude, or stirred at 600 rpm with PTFE magnetic stirrers (3.5 cm × 1.0 cm) with a MM 2A magnetic stirrer (Laboratorní přístroje, Prague, Czech Republic). A water bath was used to control the temperature. At pre-selected time intervals 300 µL aliquots were collected and filtered through 0.45 µm PTFE filters into brown vials, then immediately measured. The difference between mercury added and that remaining in the filtrate was attributed to adsorption by the sediment. Values reported are the average of three determinations. Mercury adsorption on the glassware was negligible in comparison with adsorption by the sediment.

## 2.4. Chemical analyses

Sediment S, P, Si, Mn, Fe, Mg, Al and Ca contents were determined by ICP-OES after fusion and acid digestion. Sediment (0.25 g) was mixed with 0.75 g of Spectromelt A20 (Merck, Germany) in a Pt dish and fused for 15 minutes. After cooling the melt was dissolved in 100 mL 0.7 M $HNO_3$ (Merck, Germany) and analyzed by a JY 170 Ultrace ICP-OES spectrometer (Jobin Yvon, France) with laterally viewed plasma (15 mm above induction coil). Conditions were: generator 40.68 MHz (crystal controlled); power input 1200 W; argon gas flows (L $min^{-1}$): outer 12.0, intermediate 0.6, sheath 0.2, carrier 0.6; 1 m Czerny-Turner monochromator (for S and P); Paschen-Runge polychromator (for Si, Mn, Fe, Mg, Al, Ca); spectral lines S 181.978 nm, P 213.618 nm, Si 251.611 nm, Mn 257.610 nm, Fe 259.940 nm, Mg 280.274 nm, Al 308.215 nm, and Ca 393.366 nm.

A TruSpec CHN Analyser (LECO, St. Joseph, MI, USA) was used to determine sediment total carbon and nitrogen. Sample (0.3 g) was directly weighed into a combustion boat and automatically inserted into the CHN Analyzer. Combustion temperature was 950°C. Accuracy was controlled by analyses of reference materials 502-082 and 502-062 with declared contents of N 2.45%, C 45.81% and N 0.097%, C 0.84%, respectively.

Cation exchange capacity (CEC) was determined by Mehlich 3 extraction. The sediment pH was determined in a 1:5 sediment/solution ratio with 0.01 M $CaCl_2$ [14].

Triplicate 100 µL samples were analyzed for total mercury concentration using an Advanced Mercury Analyzer AMA 254; the average was taken as the mercury concentration.

The same instrument was used for sediment total mercury determinations concentrations. Homogenized solid samples were directly weighed (*ca.* 100 mg) into combustion boats and automatically inserted into the instrument. The samples were dried at 120°C for 90 s and thermally decomposed at 550°C for 180 seconds under an oxygen flow. The selectively trapped mercury was released from the amalgamator by brief heating and quantified (measuring cycle, 60 s) as $Hg^0$ by atomic absorption spectrometry at 253.65 nm.

The detailed method of mercury species determination is described elsewhere [15]. To summarize: 1.5–3.0 g of sediment sample was extracted for 10 min (6 M HCl + 0.1 M NaCl) in a high-pressure microwave digestion unit (Ethos SEL, Milestone, Italy). After filtration (paper No. 389, 12.5 cm) the filtrates were injected into the HPLC/CV-AFS (HPLC: Perkin Elmer, Norwalk, USA; AFS: P.S. Analytical Ltd., Orpington, UK). The mercury species were separated on a Hypersil BDS C18 column (3 µm particle size, 2×125 mm, Agilent, Palo Alto, CA, USA). Isocratic elution was performed at 0.15 mL $min^{-1}$ with a mobile phase containing 7% (v/v) CH3OH and 0.05% (v/v) 2-mercaptoethanol in pH 5 acetate buffer. $CH_3OH$ content was increased to 100% at 15 min. Accuracy was controlled by analyses of sediment standard reference material CRM 580. The results are presented in Table 1.

# 3. Results And Discussion

## 3.1. Effect of movement of sediment/water mixture

The reaction of mercury species with sediment involves both chemical reactions and diffusion. Diffusion is often the rate-limiting step of adsorption in static systems. Three systems (static, agitated and stirred) imitate movement in aquatic ecosystems. The static system imitated pond ecosystems while the agitated and stirred systems imitated rivers. Movement of the sediment/water mixture increased both adsorption rates and amounts in the order: static < agitated ≤ stirred systems (Fig. 1). Increasing intensity of sediment/water mixture movement increased both rates and amounts of adsorption, showing that agitation facilitates access to adsorption sites.

## 3.2. Effect of sediment to solution ratio

Changes in the sediment/solution ratio (from 1:12.5 to 1:100 keeping the initial mercury concentration constant at 20 µg $L^{-1}$ ) did not alter the adsorption of any mercury species. On the other hand, reducing the amount of sediment decreases adsorption due to the reduction of surface area and number of binding sites. The quantity of adsorbed mercury species is controlled by sediment surface area and number of binding sites rather than sediment/solution ratio.

**Table 1.** Sediment chemical analyses

| **Sample**[a] | **S** | **C** | **N** | **P** | **Si** | **Mn** | **Fe** | **Al** | **Ca** | **Mg** | **pH** | **CEC** | **$MeHg^+$** | **$Hg^{2+}$** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | **[%]** | | | | | | | **[mmol $kg^{-1}$]** | **[mg $kg^{-1}$]** | |
| Jihlava | 0.04 | 0.69 | 0.07 | 0.33 | 63.5 | 0.10 | 5.34 | 12.0 | 2.91 | 4.48 | 6.63 | 141 | 0.004 | 0.052 |
| ZL806 | 0.21 | 2.17 | 0.24 | 0.23 | 68.4 | 0.09 | 3.71 | 9.50 | 1.61 | 1.04 | 7.33 | 344 | 0.005 | 0.115 |
| ZL1306 | 0.46 | 3.53 | 0.26 | 0.39 | 66.4 | 0.07 | 3.89 | 9.24 | 2.29 | 1.04 | 7.30 | 428 | 0.01 | 0.314 |
| ZL1506 | 0.11 | 1.82 | 0.16 | 0.20 | 70.1 | 0.12 | 4.41 | 10.6 | 1.69 | 1.34 | 7.04 | 305 | 0.012 | 0.344 |
| ZL1606 | 0.30 | 1.75 | 0.16 | 0.11 | 75.0 | 0.06 | 3.24 | 8.40 | 0.77 | 0.86 | 6.50 | 268 | <LOD | 0.059 |

*R.S.D. values (n = 3) are: S 0.17–9.30%, C 0.19–1.96%, N 1.79–8.06%, P 0.73–2.80%, Si 0.1–1.5%, Mn 0.07–1.90%, Fe 0.24–1.8%, Al 0.01–1.60%, Ca 0.07–2.40%, Mg 0.58–1.90%, CEC 5.08–8.25%,* $MeHg^+$ *4.80–7.53%,* $Hg^{2+}$ *5.38–8.54%)*

[a] *Jihlava river - [49°5´55.165´´N, 16°11´45.962´´E], Morava river - two samples ZL1606 [49°4´2.281´´N, 17°26´16.33´´E], ZL1306 [49°10´58.071´´N, 17°31´3.15´´E], Dřevnice river - sample ZL 806 [49°12´31.545´´N, 17°33´33.231´´E] and the Čerťák cutoff of the Morava river – sample ZL 1506 [49°4´5.746´´N, 17°26´11.767´´E])*

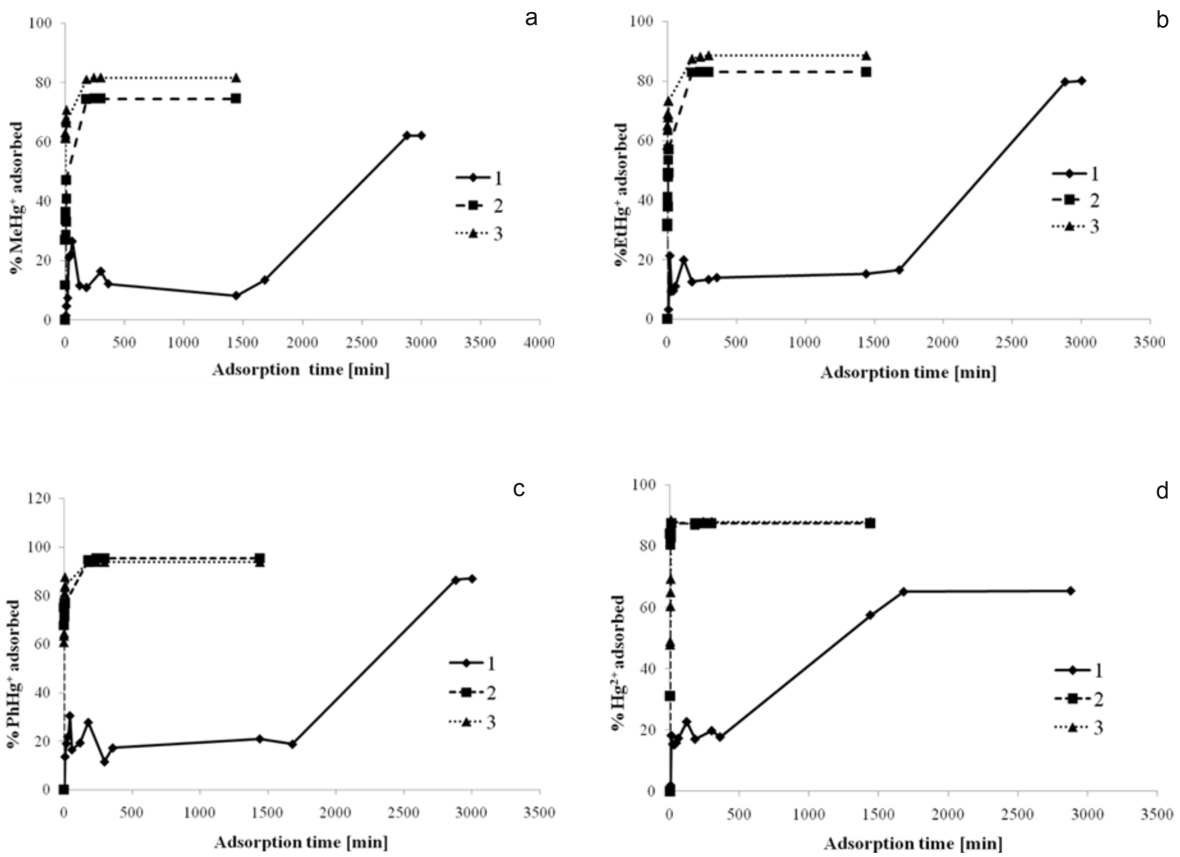

**Figure 1.** Effect of sediment/water mixture movement for (1) static system, (2) agitated system, (3) stirred system. 20 g of ZL 1606 sediment, T= 22.3°C, 250 mL of water, pH 5.2, Hg concentration 0.2 mg L$^{-1}$ ; stirred system

## 3.3. Effect of mercury species concentration

The ratio between adsorbed mercury and that remaining in solution can be represented by the Freundlich equation, which assumes that the mercury concentration in sediment is proportional to that in solution [4]. However, the expected effect of concentration changes (20 and 50 μg L$^{-1}$ ) on the quantity of mercury adsorbed was not observed (samples Jihlava and ZL1306). Mercury concentration in sediment increased only until all surface binding sites were saturated. Complete saturation occurred at 0.2 mg L$^{-1}$ mercury species.

Increasing mercury concentration from 20 to 50 μg L$^{-1}$ extended the equilibrium adsorption time for organic mercury species from 60 to 1440 min. For Hg$^{2+}$ it increased from 5 to 60 min. This can be explained by a slow adsorption step followed by a fast adsorption step. Yin *et al.* [4] described a reverse observation and characterized the adsorption kinetics by a biphasic pattern - a fast step followed by a slow step. A decrease in concentration increased the equilibration time. The dependence of the adsorption rate on Hg$^{2+}$ concentration was explained by diffusion, which has been frequently reported as rate-limiting for metal adsorption. However, our experiments were performed in stirred systems, which significantly reduced limitations due to diffusion. With increasing concentration, the most active (strong) adsorption sites become saturated first (fast step) and the less active (weaker) binding sites dominate later (slow step).

## 3.4. Effect of temperature

Higher temperature increased only the rate of adsorption, not the quantity. When the temperature of the sediment/water mixture was increased from 4.5 to 60°C, equilibration time in an agitated system decreased from 1440 min to 120 min (organomercury species) and from 7 min to 2 min for Hg$^{2+}$ (Fig. 2). Temperature also increased diffusion in a static bioreactor. In comparison with agitated and stirred systems, the static system showed the greatest reduction of equilibrium time (for organomercury species from 2880 min to 1440 min and from 1680 min to 900 min for Hg$^{2+}$). Mercury adsorption

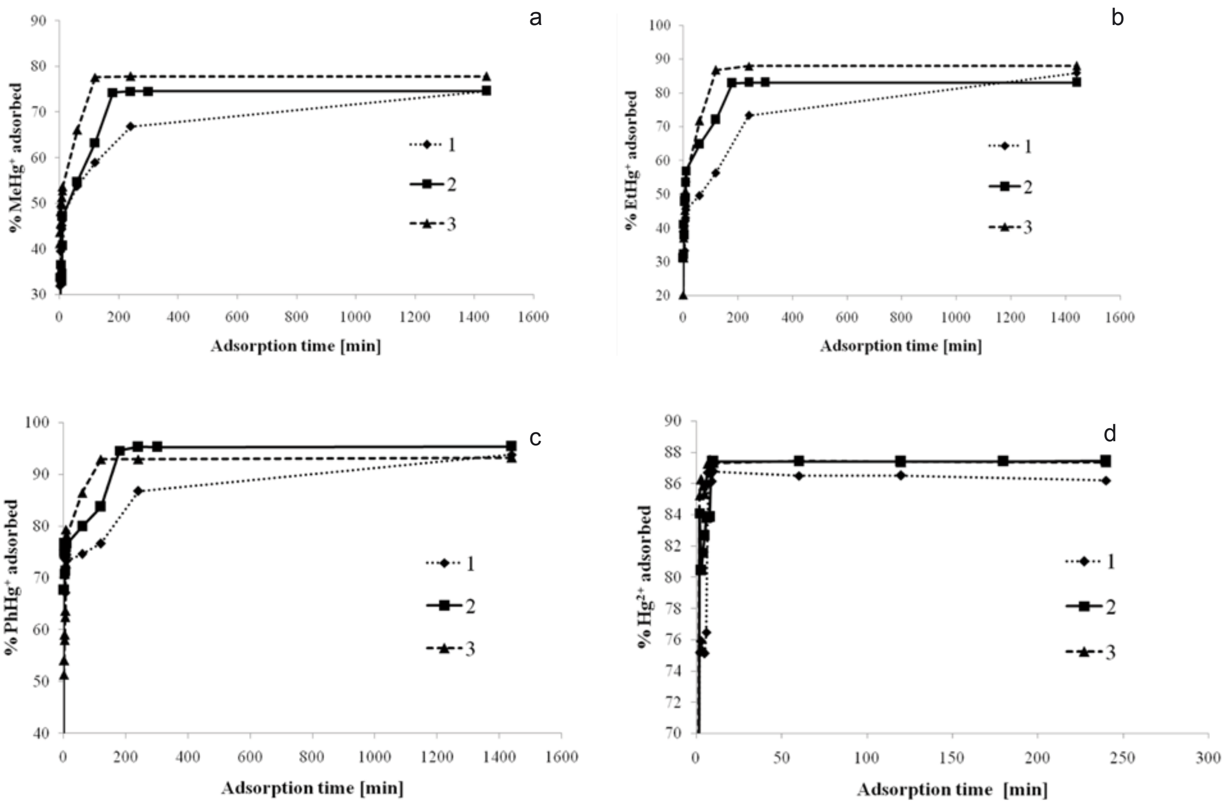

**Figure 2.** Effect of temperature for (1) static system, (2) agitated system, (3) stirred system (agitated system, 20 g of ZL 1606 sediment, 250 mL of water, pH 5.2, Hg concentration 0.2 mg $L^{-1}$ )

in real water ecosystems could be influenced by season temperature changes in the same manner. Schuhmacher *et al.* [16] observed that mercury concentration in water and sediment was lower in summer than in winter, but did not investigate adsorption rate. Their results were explained by increased microorganism activity and faster bio-transformations at elevated temperature.

## 3.5. Effect of pH

The effect of pH on $Hg^{2+}$ and $MeHg^+$ adsorption has been described [7,17-21], but little information on its effect on $PhHg^+$ or $EtHg^+$ is available. Adsorption as a function of pH for static and agitated systems is shown in Fig. 3. The relationships have similar shape for all mercury species, but the maxima differ. The same maxima were observed for agitated and stirred systems. For $MeHg^+$ and $EtHg^+$ the maxima (82-93% and 85-91% for static and agitated systems) occurred over the narrow pH range 3-4. For $PhHg^+$ the corresponding maxima (90% and 95%) were located over the broad range of 3 – 10, due to its highly non-polar structure. The adsorption maxima for $Hg^{2+}$ (94% and 97%) were observed at pH ~ 3. When the pH was adjusted with $HNO_3$ instead of HCl, about 12% more mercury was adsorbed. Reduced adsorption at lower pH values was attributed to proton competition and to a smaller extent (when using HCl for pH adjustment) to the effect of chloride ions, which form soluble chloro-complexes [7,19,20]. Reductions in adsorbed mercury at higher pH are attributed to: i) complexation of mercury species with organic ligands, since their chelation ability increases with pH [20], ii) increased formation of $Hg(OH)_2$ or RHgOH, which are poorly adsorbed [7,20], and iii) change of sediment surface potential [17,19].

## 3.6. Effect of anions

Inorganic and organic ligands in solution exert a considerable influence on mercury adsorption on soil and sediment, including kaolin, goethite *etc*. The effect of chloride on $Hg^{2+}$ and $MeHg^+$ adsorption has been described [3,7,13,17-20], but little information describing the effect of other anions is available. Thus, the effects of $Cl^-$, $SO_4^{2-}$, sulfide and phosphate at 0.2 g $L^{-1}$ were evaluated.

Despite the expectation that adsorption will be markedly lower in the presence of chloride ions due to $HgCl_4^{2-}$ and RHgCl formation [13], this hypothesis was

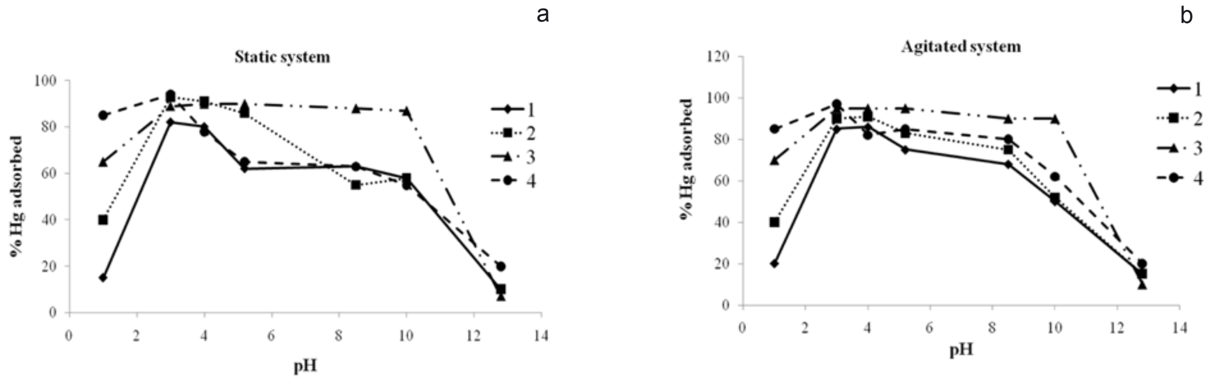

**Figure 3.** Effect of pH (static system and agitated system, 20 g of ZL 1606 sediment, 250 mL of water, Hg concentration 0.2 mg $L^{-1}$ , T = 22.3°C); (1) $MeHg^+$, (2) $EtHg^+$, (3) $PhHg^+$, (4) $Hg^2$

not confirmed. Organomercury adsorption was not markedly influenced by NaCl addition at pH 5.2. The adsorption of $Hg^{2+}$ was about 11% higher in the presence of 0.2 g $L^{-1}$ NaCl and an increase in $Cl^-$ concentration to 10 g $L^{-1}$ had little effect (Fig. 4). Similar results for pH 3 were reported by Yin *et al.* [17]. They reported that at neutral or alkaline pH, only a small amount of chloro-complexes formed, and adsorption largely depended on the balance between the interaction of other mercury species with the soil surface and complexation with dissolved organic matter. Barrow and Cox [19] also reported that the effect of chloride varied with the mercury concentration. Some authors [7,19] reported that $Cl^-$ decreased Hg adsorption at low pH, but Yin *et al.* [17,20] found that the effect of $Cl^-$ on Hg adsorption by soil at acid pH depended on soil organic matter content.

The adsorption of mercury in the presence of 1 g $L^{-1}$ $Cl^-$ was also pH dependent. We tested only three pH values (1, 5 and 12). The addition of 1 g $L^{-1}$ $Cl^-$ at very low or very high pH did not affect the quantity of mercury adsorbed, but equilibrium was delayed about 60 min. No effect of $Cl^-$ on adsorption was observed at high pH since methylmercury hydroxo species predominate [17,20]. The largest adsorption was observed at pH 5 for all species. The effect of $Cl^-$ is very complex and depends on many parameters (*e.g.*, mercury form and concentration, chloride concentration, sulfide concentration, sediment organic matter content, pH, *etc.)*.

Sulfate anions at pH 5.2 decreased the organomercury adsorption about 15-25% (Fig. 4), but did not influence the quantity of $Hg^{2+}$ adsorbed. However, the $Hg^{2+}$ equilibration time was markedly longer (from 2 min to 60 min) in the presence of 0.2 g $L^{-1}$ $SO_4^{2-}$.

A reverse effect was observed in the presence of sulfide; it decreased $Hg^{2+}$ adsorption at pH 5.2 by about 67%, but did not influence organomercury adsorption. The equilibration of $Hg^{2+}$ was delayed from 2 min to 60 min by 0.2 g $L^{-1}$ sulfide (Fig. 4) just as for 0.2 g $L^{-1}$ $SO_4^{2-}$. $Hg^{2+}$ adsorption also markedly decreased (about 29%) in the presence of sulfide at pH > 10 (Fig. 5). Inorganic mercury ($Hg^{2+}$) probably formed very stable non-adsorbing species in excess sulfide in the pH range 5.2-12, which decreased $Hg^{2+}$ adsorption. The formation of mercury sulfide was not observed in strongly acid media; sulfate did not influence the adsorption of any mercury species at pH ≤ 1, but equilibration of $Hg^{2+}$ was delayed about 8 min. Phosphate had no effect.

## 3.7. Effect of cations

The presence of cations in an aqueous ecosystem may also influence mercury adsorption on sediments. However, cations do not complex with mercury species. They probably affect adsorption via competition for active sites and precipitation of sparingly soluble hydroxo-complexes at alkaline pH. The effect of 0.2 g $L^{-1}$ $Ca^{2+}$, $Zn^{2+}$, $Mn^{2+}$, $Al^{3+}$ or $Fe^{3+}$ was investigated.

Cations in the bioreactor at pH 5.2 either slowed adsorption ($Ca^{2+}$, $Al^{3+}$) or reduced total adsorption ($Zn^{2+}$, $Fe^{3+}$). $Hg^{2+}$ equilibration was delayed about 58 min in 0.2 g $L^{-1}$ $Ca^{2+}$, but organomercury adsorption was not affected. The reverse result was observed in the presence of $Al^{3+}$. The equilibrium organomercury concentration was established about 57 min later but $Hg^{2+}$adsorption was not affected by 0.2 g $L^{-1}$ $Al^{3+}$. The presence of 0.2 g $L^{-1}$ $Zn^{2+}$ or $Fe^{3+}$ reduced adsorption of all mercury species by about 4-30% or 12-20%, respectively (Fig. 6). This can be explained by competition for adsorption sites.

$Fe^{3+}$, $Mn^{2+}$, $Al^{3+}$ (0.2 $gL^{-1}$) in strongly alkaline medium pH > 10) increased sediment $Hg^{2+}$ adsorption by about 15%, 20% and 10%, respectively. This can be attributed either to the decreased organic matter solubility caused

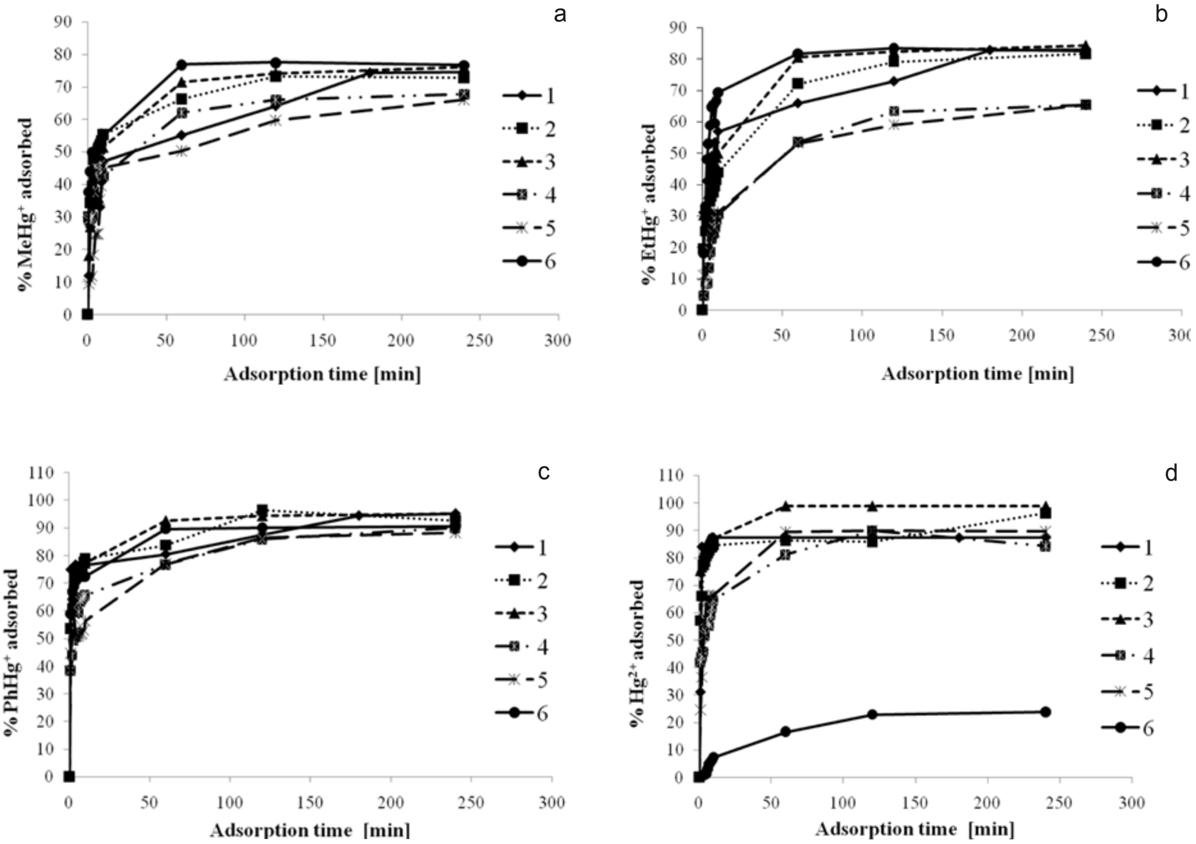

**Figure 4.** Effect of anions (agitated system, 20 g of ZL 1606 sediment, 250 mL of water, pH 5.2, Hg concentration 0.2 mg L$^{-1}$ , T = 22.3°C); (1) without anion addition, (2) 0.2 g L$^{-1}$ NaCl, (3) 10 g L$^{-1}$ NaCl, (4) 0.2 g L$^{-1}$ sulfate, (5) 0.05 g L$^{-1}$ sulfate, (6) 0.2 g L$^{-1}$ sulfide

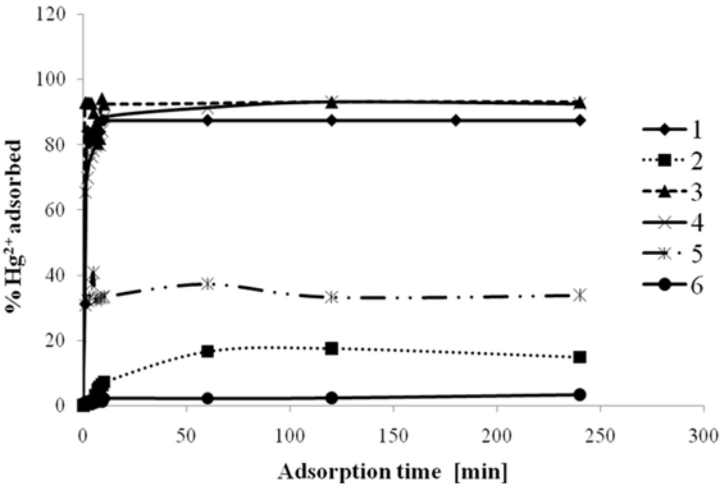

**Figure 5.** Effect of sulfide at different pH on Hg$^{2+}$adsorption (agitated system, 20 g of ZL 1606 sediment, 250 mL of water, Hg concentration 0.2 mg L$^{-1}$, T = 22.3°C) ; (1) pH 5.2, without sulfide, (2) pH 5.2, 0.2 g L$^{-1}$ sulfide, (3) pH 1, without sulfide, (4) pH 1, 0.2 g L$^{-1}$ sulfide, (5) pH 12, without sulfide, (6) pH 12, 0.2 g L$^{-1}$ sulfide

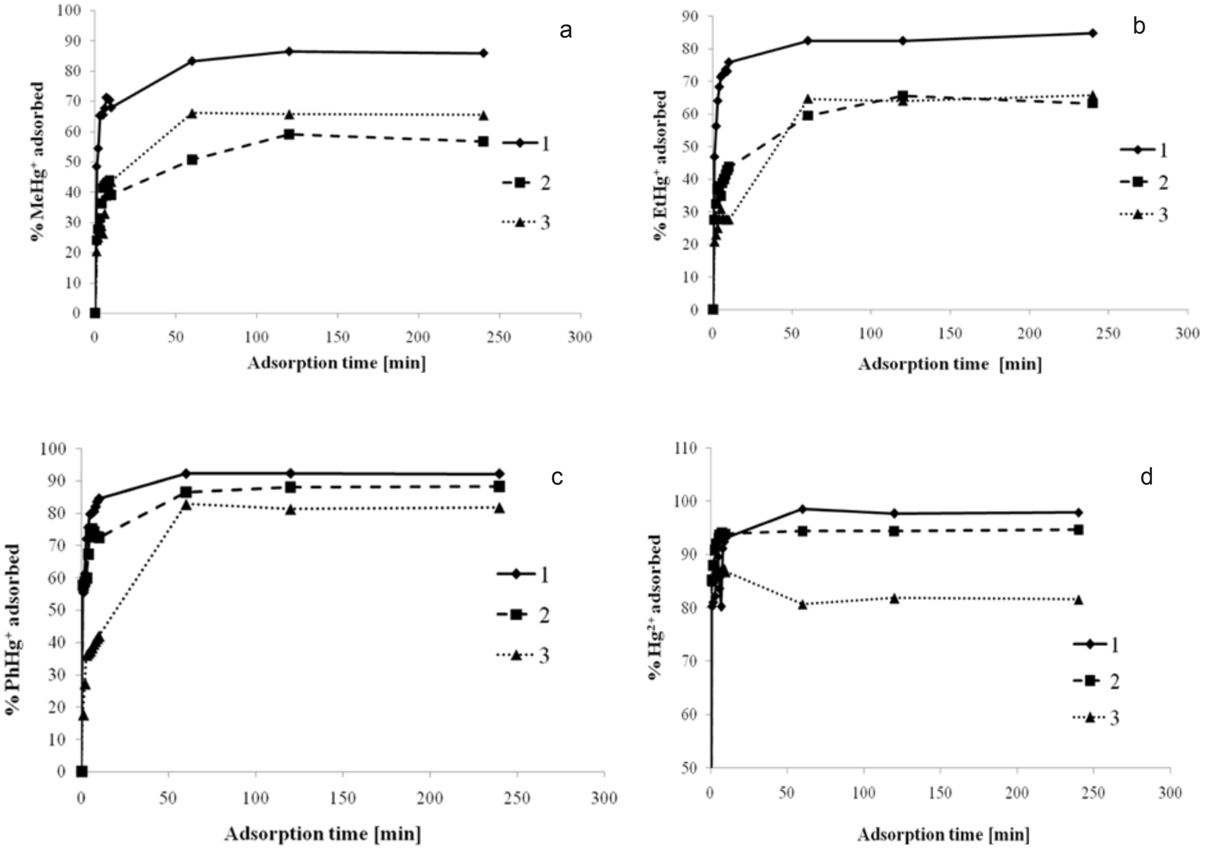

**Figure 6.** Effect of $Zn^{2+}$ and $Fe^{3+}$ at pH 5.2 (agitated system, 20 g of ZL 1606 sediment, 250 mL of water, pH = 5.2, Hg concentration 0.2 mg L$^{-1}$, T = 22.3°C); (1) without cation addition, (2) 0.2 g L$^{-1}$ Zn2+, (3) 0.2 g L$^{-1}$ $Fe^{3+}$

by cations as noted by Yin *et al.* [20] for $Ca^{2+}$, or to precipitation of hydroxo-complexes, which have large adsorption capacity. Regnell *et al.* [22] observed a substantial decrease in mercury mobility in the presence of iron and manganese hydroxides, probably due to their large surface area and high adsorption capacity. This effect was not observed for organomercury species. Based on the available results, we are unable to draw definite conclusions.

## 3.8. Effect Of Urea, Thiourea And L-Cysteine

Mercury has a strong affinity for sulfur. We tested the effects of the sulfur containing compounds thiourea and L-cysteine on sediment mercury adsorption at pH 5.2.

Organomercury adsorption decreased about 2-8% in 0.2 g L$^{-1}$ urea and about 6-20% in 0.2 g L$^{-1}$ thiourea. This reduction was not observed for $Hg^{2+}$. The presence of urea or thiourea had little effect on all absorption rates. In 0.2 g L$^{-1}$ L-cysteine equilibration of all mercury species was delayed about 58 min compared with thiourea, and the organomercury adsorption decreased about 10-25% (Fig. 7). Compounds containing S-H groups keep organomercury species in solution for much longer time due to their strong affinity for Hg. However, $SO_4^{2-}$ decreased organomercury adsorption as well as did L-cysteine, and sulfide decreased $Hg^{2+}$adsorption much more than S-containing compounds. Facile sediment adsorption of Hg-cysteine explains this.

## 3.9. Effect Of Sediment Composition

It is well known that sediment composition plays an important role in mercury adsorption, although this has been chiefly examined quantitatively for soil organic matter [23]. Positive correlations were found between C, N, S contents as well as cation exchange capacity (CEC) with mercury adsorption (R = 0.45-0.66, 0.56-0.89, 0.45-0.61 and 0.55-0.73, respectively). Increasing C, N and S contents increased adsorption since more functional groups (*e.g.* -COOH, -SH, $-NH_3$ , *etc.*) and thus adsorption sites are available. Increasing the

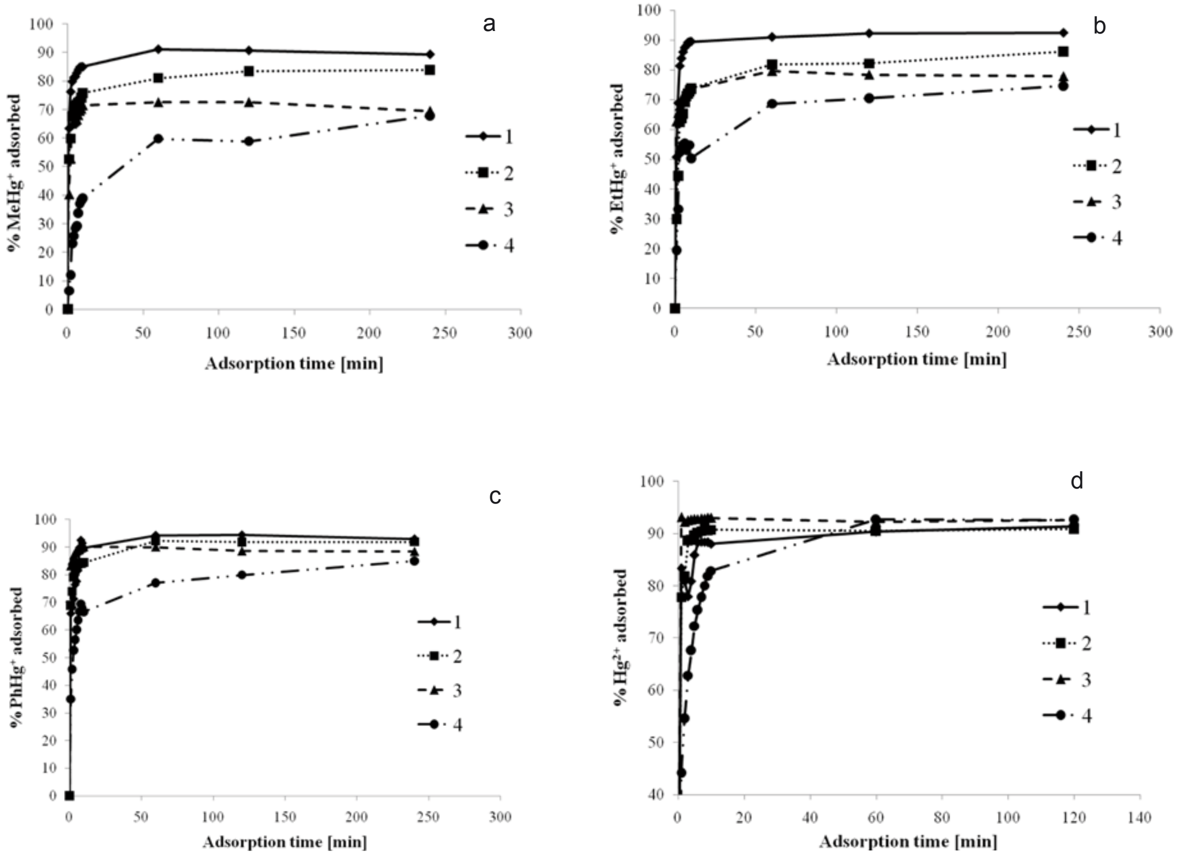

**Figure 7.** Effect of urea, thiourea and L-cysteine (agitated system, 20 g of ZL 1606 sediment, 250 mL of water, pH 5.2, Hg concentration 0.2 mg L$^{-1}$, T = 22.3°C); (1) without S-compound, (2) 0.2 g L$^{-1}$ urea, (3) 0.2 g L$^{-1}$ thiourea, (4) 0.2 g L$^{-1}$ L-cysteine

sediment Al and Fe decreased adsorption; R ranged from -0.63 to -0.90 and from -0.65 to -0.86. Competitive occupation of adsorption sites by aluminum or iron ions is responsible.

## 4. Conclusions

Sediments are sensitive indicators of mercury contamination of the aquatic ecosystem. The behavior of mercury strongly depends on its chemical form and on various physical, chemical and biological factors. Thus knowledge of adsorption/desorption behavior under different conditions is important in understanding the mercury bio-geochemical cycle.

Adsorption of mercury on sediment varies markedly among individual mercury species. Some abiotic parameters influenced only the rate of adsorption (temperature, mercury species concentration, composition of aqueous media – *e.g.* presence of $Ca^{2+}$, $Al^{3+}$); other abiotic parameters influenced the quantity adsorbed (pH, compositions of sediment and aqueous media – *e.g.* presence of $SO_4^{2-}$, $S^{2-}$, $Zn^{2+}$ or $Fe^{3+}$ at pH 5.2; presence of $Fe^{3+}$, $Mn^{2+}$ or $Al^{3+}$ in strongly alkaline medium, *etc.*).

Finally, sediment adsorption/desorption of mercury species is a very complex process that depends on a number of physico-chemical parameters. The article presents new and more complex information about mercury adsorption on river sediments. Extension to further observations of mercury photo- and biotransformation and bioaccumulation in the water environment is desirable. A multifactor experiment to develop a more detailed description of mercury species adsorption is in progress [24].

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