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On the leaching of mercury by brackish seawater from permeable barriers materials and soil

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ABSTRACT

Soils at former pulp, paper and chemical plants in the subarctic (boreal) zone, including Canada, Scandinavia, Russia, and parts of the USA, are often contaminated with organic pollutants and heavy metals, of which mercury is one. The soil- and ground-water at these sites is often rich in dissolved organic matter (DOM), particularly fulvic substances. Permeable barriers are sometimes used to limit the migration of pollutants with groundwater and protect nearby aquatic environments. These are installed downstream of the source, generally close to the receiving water body. In cases when such barriers have been installed close to the sea, concerns have been raised that the seawater may back-flush the barrier and release mercury, often a key contaminant, in the form of stable chloride complexes.

Intrusion of seawater into coastal groundwater reservoirs has previously been shown to result in dissolution of mercury from soil. Less is known about the ability of brackish water, present in estuaries or brackish seas, to mobilize mercury from soil or from barrier materials. We therefore investigated the effect of artificial brackish seawater (6.3‰ salinity) on the sorption and desorption of mercury from different barrier materials (activated carbon, fly ash, lignite, torrified material, peat, and iron powder).

The mercury was found to be associated with the high molecular weight fraction of groundwater DOM and it was concluded that the mercury was removed (sorbed) as relatively strong DOM-complexes. Chloride ions did not seem to form aqueous complexes with mercury to any great extent and artificial brackish seawater did not desorb mercury from the contaminated soil or from the studied barrier materials.

Introduction

In many parts of the world, health authorities are becoming increasingly concerned about the effects of heavy metals on environmental and human health [1]. Unlike organic contaminants, metals do not undergo microbial or chemical degradation, and these elements persist, in their original quantities, for a long time after their introduction into soils [2]. Some of them also accumulate in living organisms, causing various diseases and disorders [3]. Mercury is one of the most well-known heavy metal environmental pollutants because of its toxicity and its ability to bioaccumulate in the food chain [4]. It has often been used in chlor-alkali synthesis, the wood pulping industry, technical instruments (thermometers, barometers), electrical equipment (batteries), dentistry, paints, and military applications [5], inevitably leading to soil and groundwater contamination. To protect the general population, national governments have set maximum contaminant levels in drinking water (USA, 0.002 mg L^{-1}; EU, 0.001 mg L^{-1}; Sweden, 0.001 mg L^{-1}) [6–8] and initiated remedial efforts to mitigate the problems associated with Hg contaminated soils and groundwater.

In order to support such studies, it is important to understand the behavior of mercury. The adsorption and desorption of mercury in soil is mainly controlled by processes involving complexation, the most important ligands in solution being OH^-, Cl^-, and organic anions. Since the stability of aqueous Hg (II) complexes, such as $HgCl_2$ (aq) and $Hg(OH)_2$ (aq) is rather high, association of Hg to these ligands leads to increased mobility. However, mercury also has a very high affinity to sulfur, which explains the strong binding of Hg to dissolved organic matter and also the stability of inorganic HgS [9]. To make the picture even more complicated, mercury can also bind with humic acids [10]

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which may either prevent mercury emission from the soil [11], if the humic acids have low mobility, or lead to leaching of mercury, if the acids have high mobility. Thus, the composition and relative mobility of various pools of soil organic matter determine the behavior of Hg in soils [12].

Groundwater polluted with mercury can be a source of coastal water contamination [13,14]. A way to prevent this and treat polluted groundwater is to install a permeable barrier (PB) downstream of a contamination source. This is often more cost-efficient than pump-and-treat solutions or excavating and safely storing contaminated soil; and it has been shown to work even in extreme environments [15,16]. The efficiency of the materials depends both on the sorbent material and the groundwater composition. Several sorbents have been used for mercury removal from aqueous solution (mercury uptake range presented in brackets); these include zeolites (16–43 $mg\,g^{-1}$) [17], clay minerals (0.01–0.04 $mg\,g^{-1}$) [18], ion-exchange resins (216–368 $mg\,g^{-1}$) [19], activated carbon (0.36–0.80 $mg\,g^{-1}$) [20,21], peat (49–123 $mg\,g^{-1}$) [22,23], and zero-valent iron (12–448 $mg\,g^{-1}$) [24]. The main removal mechanisms of these materials are suggested to be ion exchange, adsorption, surface complexation on functional groups and amalgamation.

The stability of the captured compound, in this case mercury, is a crucial factor for the long-term efficiency of a PB. Factors such as pH and contents of competitive organic acids and cations influence mercury sorption by PBs [25]. Concerns have been raised that PBs located close to the sea may be exposed to elevated chloride concentrations, which could lead to mercury desorption. Seawater intrusion into coastal aquifers in Tuscany, Italy, has been shown to be responsible for dissolution of mercury minerals present in the soil and tainting of groundwater [26,27]. Studies of marine sediments provide support for such an idea. It has been shown that increased salinity levels cause increased desorption of Hg from river sediments [28] and that the release increases drastically above a $C1^-$ concentration of 0.02 M [29]. One possible explanation is that mercury is desorbed from metal(hydr)oxides at increasing concentrations of chloride through the formation of soluble Hg–Cl complexes [30]. In contrast, however, studies by Lamborg et al. [31] indicate that the levels and composition of groundwater DOM exert a greater impact on mercury speciation than chloride.

It is plausible that brackish water also may desorb mercury from contaminated soils, sediments or barrier materials used to restrict the transport contaminated groundwater. The current study was conducted to support a case study, in which DOM-rich and Hg polluted groundwater is to be treated by a PB located on the shore of the brackish Bothnian Sea. The sorption of mercury to different PB materials was investigated using pure water and groundwater extracted from the site. Sequential desorption was then performed using artificial seawater to investigate the mercury leachability. Additional experiments were performed to investigate how Hg is distributed among various size fractions of DOM. Together, the experiments provide improved insights into the speciation of Hg in DOM-rich groundwater, the sorption strength of mercury and DOM to various sorbents under varying salinity conditions, and the extent to which chloride ions interact (complex) with sorbed mercury. The implications of the results for the location and design of PBs are also discussed.

Material and methods

Sampling of soil and water and preparation of artificial seawater

In this work, we studied groundwater extracted from a large industrial area in Northern Sweden on the shore of the Bothnian Sea. This area has a long history of industrial exploitation, including: pulp and viscose production, chlorine production (for bleaching), production of fine chemicals, and storage of fuel oil and timber. Inevitably, the groundwater has been contaminated with heavy metals and organic pollutants. It also contains high levels of DOC (>100 $mg\,L^{-1}$). However, the high concentrations of DOC are typically found throughout the northern subarctic boreal region (in remote as well as industrialized areas).

The groundwater extraction well was situated in an area where a PB is most likely to be installed. Groundwater was collected as grab samples and was transferred to clean PE bottles. A soil sample was taken in the immediate vicinity of the extraction well before being transferred to a clean PE bag. Samples were taken from an approximate depth of 1 m. Upon arrival in the laboratory, the collected water was filtered through 0.45 μm filters (Minisert, Hydrophilic) and the pH was measured. The water and the soil samples were stored in a cool room (4 °C ± 2 °C).

Artificial seawater (ASW) with a salinity of 6.3‰ (Bothnian Sea concentration) was prepared according to [32,33], except that hydrogen borate and strontium chloride were excluded since it is unlikely that the presence of strontium and borate would affect the speciation of Hg(II). The ASW was prepared using sodium chloride (Merck, Germany), sodium sulfate (Merck, Germany), potassium chloride (Scharlab, Spain), sodium hydrogen carbonate (VWR, Belgium), and potassium bromide (Fisher Scientific, UK). The salts were dissolved in ultrapure water and the pH of the water was adjusted to 7.0 with 3% NH_4OH (Scharlab, Spain).

Saturation of sorbent materials by mercury

The sorbent materials used in this study are listed in Table 1. The sorbents were selected based on the cost of the materials and (expected) mercury sorption strength and capacity. The selected sorbents covered a range of sorption mechanisms, which possibly are affected differently by presence (competition) of chloride ions. Saturation of sorbents by mercury was performed using two water solutions with the same concentration of Hg^{2+}: 0.1 $mg\,L^{-1}$ (prepared from mercury(II) nitrate; Sigma–Aldrich, USA). One solution was made using ultrapure Milli-Q water and the other was made using groundwater from the industrial site (with a DOC concentration of 500 $mg\,L^{-1}$).

Ten grams of each material was added to a 1000-mL glass flask and filled with 500 mL of 0.1 $mg\,L^{-1}$ Hg^{2+} solution. It is known that the properties of zero-valent iron (ZVI) are influenced by oxygen content in the water [34–36]. For this reason we saturated the ZVI under aerobic conditions (as for all other materials) and anaerobic conditions (using an argon purge). All flasks were shaken for 7 days at 20 °C. Initial pH of the solutions was 7.0. Samples were then taken for analyses of Hg and DOC content as described below. Adsorption q ($mg\,kg^{-1}$) was calculated as follows:

Table 1
Materials used for mercury leaching test.

Material	Supplier
Activated carbon, Norit GAC 1240 W	Sigma–Aldrich
Fly ash	Hörneborgsverket, Övik Energy AB, Sweden
Lignite	Mátrai Erőmű, Bükkábrány, Hungary
Torrefied material (pyrolyzed pine stemwood pellet; solid char 47%)	In house
Peat	Hörneborgsverket, Övik Energy AB, Sweden
Iron, HCA-150N cast iron powder	Hepure Technologies Inc., USA