Mobilization of arsenic, lead, and mercury under conditions of sea water intrusion and road deicing salt application

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ABSTRACT

Water geochemistry data from coastal aquifers of Bangladesh and Italy, a salted watershed of New Jersey, US, and complexly designed salt-solution injection experiments in the laboratory were collected and analyzed to study the geochemical mechanisms that mobilize As, Pb, and Hg under varied salting conditions in a watershed. Overall, increased NaCl-concentrations in aquifers and soil are found to increase the release of Pb and Hg in water through the combined effects of dispersion of organic matter and clay minerals by hydrated Na\textsuperscript{+}, ion exchange, and complexation by Cl. Reducing environments and possible desorption by hydrated Na\textsuperscript{+} are found to lead to an increase of As-concentration in water. However, the application of a pure NaCl salt solution in the column injection experiment was found to release less As, Pb, and Hg initially from the soil and delay their concentration increase, when compared with the application of CaCl\textsubscript{2} and NaCl mixed salts (at 6:4 weight ratio). The concentration correlation dendrogram statistical analyses of the experimental and field data suggest that the release of As, Hg, and Pb into groundwater and the soil solution depends not only on the salt level and content, but also on the redox condition, dissolved organic matter contents, competitiveness of other ions for exchange sites, and source minerals. The results of this study help to explain the concentration variations of As, Pb, and Hg in groundwater in some coastal regions of Asia, Europe, and North America, where As- concentrations generally are inversely, and Pb- and Hg- concentrations positively correlated with the Cl-concentrations in a water body. With an over-exploration of coastal aquifers from increased pumping, continued sea-level rise, and increased winter deicing salt applications in salted watersheds of many inland regions, the results of this study will certainly shed some more light on the mechanisms of mobilization of As, Pb, and Hg in a coastal aquifer and in soils of a salted watershed.
Keywords: Mobilization mechanism of As, Pb, Hg; sea water intrusion; deicing salt; groundwater.

1. Introduction

As (Arsenic), Pb (lead), and Hg (Mercury) are three of the most concerned toxin metals in a water system. High As-concentrations in water can cause permanent damage to the ecosystem and is carcinogenic to people (Barringer et al. 2007; Smedley and Kinniburg 2002). Pb accumulation in the food chain can result in a negative neurocognitive outcome for animals and people (Datko-Williams et al. 2014). Elevated concentrations of Hg also have detrimental effects on microbes and invertebrates (Rundgren et al. 1992; Tipping et al. 2010).

As occurs often as an oxyanion or a neutral species and undergoes important changes in oxidation states when moving from groundwater to stream water. Elevated As-concentrations in groundwater and soil solutions are generally associated with a heightened As-source and a reducing environment that is rich in Fe-Mn oxyhydroxide (Barringer et al. 2007; Smedley and Kinniburg 2002).

Pb often occurs as a divalent cation, either free or complexed in groundwater, soil solution, and stream water. In addition to the natural supply, increased Pb-concentrations in groundwater and soil solution near roadsides have been related to anthropogenic input, dispersion of organic matter by hydrated Na$^+$ and complexation with Cl (Nelson et al. 2009; Norrström and Bergstedt 2001; Norrström and Jacks 1998).

Hg occurs in a highly complex form as either an oxidized Hg$^{2+}$ ion or a hydrolysis product Hg(OH)$_2$0 (Drever 1997). Changes of the total Hg-concentrations in stream water and soil are generally associated with its high retention and mobilization by Cl-complexation, and potential anthropogenic input at some sites in a watershed (Balogh et al. 2008; Barringer et al. 2004; Bollen et al. 2008; Doner 1978; Lumsdon et al. 1995; Scherbatskoy et al. 1998).

With rising sea levels and over-pumping along coastal aquifers, increased salinity and elevated Hg-concentrations in groundwater related to salt water encroachment were also observed (Grassi and Netti 2000; Protano et al., 2000; Barringer et al. 2007). In addition, many other studies have expressed concerns on the release of the overall trace metals Cd, Cu, Pb, Hg, and Zn to the supply of drinking water related to the growing use of deicing salt in watersheds.
in northern US, Europe, and Canada (Amrhein et al. 1994; Amrhein and Strong 1990; Backstrom et al. 2004; Bauske and Goetz 1993; Nelson et al. 2009; Norrström and Jacks 1998). The causes of elevated overall trace metal concentrations, in response to the increased salt concentrations, have been attributed to cation exchange, Cl and organic complexes, and colloid dispersions (Amrhein et al. 1994; Nelson et al. 2009). Those studies generally focused on the effect of salt application on the concentration changes of Cd, Cu, Pb, and Zn in groundwater and soil solution (Backstrom et al. 2004; Menzies and Jacks 1998; Nelson et al. 2009; Norrstrom and Jacks 1998). However, there is a lack of studies on the geochemical mechanisms that mobilizes As, Pb, and Hg from aquifer and soils under varied salting conditions.

Therefore, the purpose of this study is to examine the aqueous geochemical conditions that mobilize As, Pb, and Hg from coastal aquifers and soils in response to the salt encroachment and deicing salt applications. The examination will include analyses of geochemical data from the leachates of complexly designed column experiments, geochemical data from brackish groundwater of published articles, and our own geochemical data from highway runoff, soil solutions, and stream water in a salted watershed of New Jersey, US. Complexly designed column experiments compensate the regular NaCl-salt-only-scenario with a mixed CaCl$_2$- and NaCl- salting scenario that is common in coastal aquifers and is increasingly common in inland regions of the northern hemisphere where deicing salt is applied. Arsenopyrite and galena minerals were added into two of the experimental soil columns to mimic the elevated source of As and Pb in the aquifer.

The results of this study will help understand the geochemistry of As, Pb, and Hg release from coastal aquifers into groundwater and from soils to stream water. As such, this study will act as a critical first step in recognizing the increased threat of As, Pb, and Hg to the health of a water system (Nelson et al. 2009; Rundgren et al. 1992; Tipping et al. 2010).

2. Release of As, Pb, and Hg in Response to Salinity Change in Coastal Aquifers

Arsenic (As) related geochemistry data from three areas: Gangers, Chapai-Nawabgan, and Meghna rivers across the country of Bangladesh obtained from Reza et al. (2010a,b), Halim et al. (2010) and Shamsudduha et al. (2008) were analyzed. Though the correlations between the
concentrations of As and Cl are not all statistically significant, based on the t-test for most samples, their negative correlations are persistent (Table 1). There are also consistent negative correlations between the concentrations of As and the major common cations Na\(^+\), K\(^+\), Ca\(^{2+}\) and Mg\(^{2+}\) in the groundwater of this region which indicate that the generally high alkaline salt water intrusion into the coastal aquifer usually has an unfavorable influence on the release of As into groundwater. Further examinations of that data and the conclusions presented by these researchers also indicate that the As-concentrations are significantly and positively correlated to that of a reducing environment indicator Mn (Reza et al 2010a,b; Halim et al., 2010).

The positive concentration correlation between As and Mn has also been confirmed in studies of other regions (Barringer et al. 2007; Shamsudduha et al. 2008). In addition, Reza (2010a; b) indicates that an As-release is also facilitated by an increased dissolved organic matter content. Significant correlations between the concentrations of Si and As (correlation coefficient=0.46, t=2.93, n=33) in the Manikganj flood plain found by Shamsudduha et al. (2008) indicate that the very likely source of As in Bangladesh are the aquifers with high As-concentrations, instead of sea water, as the latter has only relatively low concentrations of dissolved silica.

From the limited data analyzed in the Chapai Nawabganj region by Rena et al. (2010a), a positive correlation between the concentrations of Cl and Pb, though not statistically significant, can be observed. This positive correlation indicates that salt water intrusion likely facilitates the release of Pb into groundwater and this fact will be further demonstrated by our experimental data in a later section.

Here we also analyzed the geochemical data of Grassi and Netti (2000) for Ansedonia and Castiglione in the Pescaia region in Italy that showed a clear relationship between concentrations of Hg and Cl (Figure 1). The correlation coefficient between concentrations of Cl (salinity of 2 to 34) and Hg (0.5 to 5.5 μg/l) was calculated as 0.88, with a t-test score of 7.8 for the 18 samples of this dataset. The correlation coefficient between Hg and all the major cations (Na\(^+\), K\(^+\), Ca\(^{2+}\), and Mg\(^{2+}\)) for groundwater samples collected by Grassi and Netti (2000)’s study are also larger than 0.88. These positive correlation coefficients indicate indeed that salt water intrusion will facilitate the release of Hg from a coastal aquifer.
3. As, Pb, and Hg Chemistry in the Salt Injection Laboratory Experiment

3.1. Injection of NaCl into regular and mixed arsenopyrite and galena soil columns

3.1.1 Setup

Four two-inch (5.08 cm) diameter columns were filled with about 480 grams of loamy soil collected from A and upper B horizons at the Centennial Lake Watershed (CLW), New Jersey (Figure 2). Two of the four soil columns contained powdered arsenopyrite (~35 grams) and galena (~70 grams) mixture to initiate the potential elevated sources of As and Pb, and two soil columns had no added minerals. The other two columns were filled with only regular soils and served as control columns.

The columns used the falling-head apparatus set-up. 0.125 and 0.25 moles of sodium chloride solutions (1100 ml in volume) were injected into each column, respectively. After the injection, low-ionic-strength water was added once or twice daily (an average of about 300 milliliter daily) with no overflow allowed.

The leachate of each soil column was collected for up to three weeks. Collection of the leachate stopped when a steady linear change of Na and Cl concentrations was reached. Concentrations of the Na, K, Ca, Mg, Al, Fe, Mn, Zn, Cu, Pb, As, Hg, Si, Cl, S, and P in the leachate were all measured by a SPECTRO Inductively Coupled Plasma (ICP) Spectrometry, which can simultaneously measure the emitted light spectrum from 165 to 770 nm. Concentrations reported in this paper are the total elemental concentrations of the dissolved and colloid adsorbed species of an element in a solution.

3.1.2. Result for injection into regular soil columns

For the injection of 0.125 moles of NaCl into the regular soil column, Na-concentrations in the leachate ranged from 27.7 to 1392.5 ppm, As-concentrations from 2.26 to 15.79 ppb, Pb-concentrations from 0.89 to 20.99 ppb, and Hg concentrations from undetectable to 5.22 ppb at the peak. For the injection of 0.25 moles of NaCl, the As-concentrations in the leachate ranged from 2.2 to 55.3 ppb, Pb-concentrations from 0.51 to 84.1 ppb, and Hg-concentrations from undetectable to 25 ppb (Figure 3).

The low numbers in the above concentration range are about the background concentrations of a corresponding element, before the salt injection and the high numbers are the peak
concentrations of the element after the salt injection started (concentration ranges depicted in the ensuing sections will follow the same convention).

Ca-, Mg-, K-, and Mn- concentrations peaked in a slightly different order, but were almost in synchronization with the peaks of Na- and Cl- concentrations in both columns, due to cation exchange. On the other hand, the concentrations of As, Pb, Hg, Fe, P, S, Al, and Si had their near lowest values, when the concentrations of Na and Cl peaked, very likely due to the masking effect to ICP sensitivity by the high intensity of Na and Cl (Pueyo et al. 2004). Their concentrations increased only, once the concentration peaks of Na and Cl had passed. Concentration-peaks of the non-common elements (Na, Ca, Mg, Ca, S, and Cl are referred as the common elements in this paper), including Si and Al, arrived later than the concentration peaks of Na and Cl, which is likely due to the late release from dispersion of organic matter and clay minerals. Flushing of the soil columns with low ionic-strength water, following the injection of NaCl, leached soluble salts from the soil column and created a sodic soil condition. Dispersion occurs in the sodic soil when swarms of loosely absorbed hydrated Na\(^+\) surround the outer-sphere complexes of soil colloids and the poorly balanced electronegative colloids repel each other (Brady and Weil 2012).

3.1.2. Result for injection into arsenopyrite and galena mixed soil columns

For the injection of 0.125 mole of NaCl solution, the Na- concentrations in the leachate ranged from 33.3 to 1324.6 ppm (Figure 4) As- concentrations ranged from 39.5 to 1621.7 ppb, and Pb-concentrations ranged from 26.68 to 137.27 ppb. The concentration peaks of As, Pb, Ca, Mg, K, Mn, and S in the leachate were almost in synchronization with that of Na and Cl. However, the delays of the concentration peaks of Hg, Fe, Al, Si, and P in the leachates were similar to their delays in the regular soil column injected with NaCl, as discussed in the previous section. Hg concentrations ranged from undetectable at the beginning of the experiment to 2.68 ppb near the end of experimental run. The synchronized increase of the As- and Pb-concentrations with that of Na and Cl was likely due to the ample supply of As and Pb from the dissolution of arsenopyrite and galena, facilitated by the influx of NaCl through cation and anion exchange and dispersion (Figure 4). Those late elevated concentrations of Hg, Fe, P, S, Al, and Si, including that of As and Pb, were likely due to the increased dispersion of organic
matter, complexation with Cl, and an increased reducing environment after prolonged water flushing.

3.2. Injection of CaCl$_2$ and NaCl mixed salt into the regular soil column

3.2.1. Setup

Approximately 480 grams of dried loamy soil collected at the same site mentioned above were added to two other two-inch (5.08 cm) diameter columns. 0.25 and 0.5 molar solutions (1100 ml in volume) at a 6:4 weight ratio of CaCl$_2$:NaCl were injected into the two soil columns, respectively. The 6:4 CaCl$_2$:NaCl weight ratio was to mimic the salt mixing composition mandated by the State of Rhode Island, USA, for its winter deicing road salt, since 1990 (Breault and Smith 2010; Sun et al. 2012). The injections were followed by a daily flushing with about 300 milliliter of low ionic strength water for three weeks, except weekends, similar to the injection of the NaCl experiment. The leachate of each soil column was collected at a regular interval during the injection period. Concentrations of the elements as listed in section 3.1 were all measured by the ICP.

3.2.2. Result

Concentrations of all elements in the leachate from the injection of both the 0.25 and 0.5 moles solutions of mixed CaCl$_2$ and NaCl at a ratio of 6:4 are always higher than those from the pure NaCl salt experiments discussed previously, and peaked almost in synchronization with that of Ca and Na (Figure 5). This synchronization of the concentration change was due to the increased exchange capacity of Ca$^{2+}$, which had been verified in other extraction studies (Meers et al. 2007; Menzies et al. 2007; Pueyo et al. 2004). Because the stocks of As, Pb, Hg, P, and Al in the soil column could be depleted by the cation exchange, desorption of Ca$^{2+}$ after the mixed salt injection, concentration increases of As, Pb, and Hg by the hydrated Na$^+$ induced dispersion was not as apparent as in the pure NaCl injection.

For the injections of 0.25 and 0.5 moles of mixed salt solutions, the Ca- concentrations in the leachates of the respective molar concentration ranged from 24.9 to 893.1 ppm and 13.79 to 3398.9 ppm, Na- concentrations from 9.5 to 2428.5 ppm and 7.42 to 5225.5 ppm, As- concentrations from 0.96 to 23.14 ppb and 0.847 to 32.23 ppb, Pb-concentrations from 0.79 to
749.2 ppb and 0.063 to 794.5 ppb, and Hg-concentrations ranged from 0.17 to 0.31 ppb and 0.45 to 3.45 ppb.

It is apparent that increased salt concentrations increase the release of metals, similar to the results from the single salt injection (Figure 4). High concentrations of Mn and Fe in the leachate proved that CaCl$_2$ is also very effective at removing the Mn and Fe oxyhydroxides which are effective adsorbents of the trace metals As, Pb, and Hg in soil particles (Tessier et al. 1979, 1996).

4. As, Pb, and Hg Chemistry in a Watershed with Large Deicing Salt Application

4.1 Runoff water samples off interstate highway

Runoff water from three transects along Interstate highway 95 in the Centennial Lake Watershed (CLW), New Jersey, US, (Figure 2) where usually a large amount of winter deicing salt is regularly applied were collected to analyze the change of metal concentrations of pre- and post-salting period during 2012-2013. Overall, the Na-concentrations were more than 266 times (6678 ppm) those of the pre-salting Na-concentration (25.1 ppm) (Table 2).

As-concentrations in the runoff water ranged from <0.5 ppb to 3.6 ppb and averaged 1.56 ppb in the three transects. Pb-concentrations ranged from undetectable to 4.4 ppb, averaged to 2.35 ppb, in the three transects. Hg concentrations were undetectable in all the samples. A possible association of the lowest As-concentrations with the highest Na-concentrations is likely due to the masking of the ICP sensitivity by the high intensity of Na, as discussed in previous sections (Pueyo et al. 2004). The higher As-concentrations (on 2/27/2013 Table 2) shown after the sodium peak had passed is likely due to the possible hydrated Na+-induced dispersion of clay and organic matter in the soil. Concentration-decreases with increasing distance away from the edge of the highway were obvious only for some common elements (Na, K, Ca, Mg, S, and Cl) (Table 2).

4.2. Stream water

The upstream As-concentrations collected in the studied CLW, New Jersey during the 2012 to 2013 measuring period ranged from 0.28 to 2.35 ppb, averaged to 1.08 ppb, with higher concentrations in the off-salting season (Figure 6). Pb-concentrations ranged from 0.44 to 2.01
ppb, averaged 0.95 ppb and Hg-concentrations ranged from undetectable to 2.00 ppb, averaged 0.593 ppb, with their highest concentrations in the salting season. Concentrations of these three elements in the downstream water ranged from 0.5 to 1.57 ppb, with an average of 1.04 ppb for As, ranged from 0.48 to 1.1 ppb, with an average of 0.84 ppb for Pb, and ranged from undetectable to 1.78 ppb, with an average of 0.47 ppb for Hg during the 2012 to 2013 measuring period. The concentration variation of downstream water has the same pattern as that of the upstream water.

4.3. Soil solutions from lysimeters

Concentrations of most elements in the soil solutions collected by the lysimeters in the same CLW, New Jersey (Figure 2) are significantly higher than the concentrations of these elements in stream water, except for that of Na and Cl (Figure 7). As-concentrations during the 2012 to 2013 measuring period ranged from 0.93 to 3.48 ppb, with an average of 2.88 ppb, for lysimeter #1, which has the most complete record. Pb-concentrations ranged from 1.21 to 1.85 ppb with an average of 2.01 ppb and Hg-concentrations ranged from undetectable to 2.55 ppb, with an average of 0.49 ppb. Because the lysimeters are located in the woods (Figure 1), where there is no input of road salt, elemental concentrations in the soil solution collected by the lysimeters reflect the elemental concentrations of the baseflow.

5. Mechanism of As, Pb, and Hg Release under Varied Salting Conditions

Relationships established between the concentrations of As, Pb, Hg and that of varied salt contents from the laboratory experiment under defined conditions help to understand the release mechanism of these three metals from a coastal aquifer and soils under varied salting conditions.

5.1. Arsenic

In the regular soil column experiment where arsenopyrite and galena were not added and NaCl-solutions were injected, two elemental groups can be identified in the concentration correlation dendrogram (Figure 8). One group represents mainly the cation exchange elements Na, Cl, Mg, and Ca. Another group represents the dispersion-weathering related elements: Fe, As, K, Mn, Si, P, Pb, and Hg, where K is related to both cation exchange and dispersion of
organic matter. In this second group, the close correlation of the As- and Fe- concentrations in the dendrogram indicates As’s strong affinity to Fe oxyhydroxides (Barringer et al. 2007; Smedley and Kinnibur 2002). The positive correlation between the concentrations of As and P implies the possible substitution of $\text{PO}_4^{3-}$ and $\text{AsO}_4^{3-}$ anionic groups in the minerals, because of their chemical similarity (Cornell and Schwertmann 2003; Tessier et al. 1996). Dispersion by hydrated Na$^+$ and a reducing condition resulting from the prolonged flushing is the likely mechanism of the elevated As- release from soil for the NaCl injection near the end of the experiment run, though the As- concentration is negatively correlated with that of the Cl in the NaCl-only salt injection experiment (correlation = -0.43, -0.58, n=22 for both columns), similar to relationship observed in the field data.

In the soil columns with arsenopyrite and galena added and a NaCl-solution injected, and the soil columns with no minerals added, but mixed-salt injected, increases of the As-concentrations in their leachates were in synchronization with the increases of Na, Ca, Mg, and K concentrations (Figures 4 and 5). The difference between As sources in the soil columns with added minerals and the soil columns with injection of mixed salt is that the As source in the former is arsenopyrite, whereas the As source in the latter is the As-adsorbents on organic matter and clay minerals, and the secondary As-minerals formed by oxidation (Smedley and Kinnibur 2002).

In the leachates of mixed salt columns, the increases of the As, Pb, and Hg- concentrations are initially larger than those of NaCl-only salt experiment and synchronized with the increases of Na and Ca-concentrations, because the divalent Ca$^{2+}$ has a much stronger desorbing ability than the monovalent Na$^+$ (Meers et al. 2007; Menzies et al. 2007). In fact, moderate to low concentrations of CaCl$_2$ have been used for that reason as a standard agent for extracting As from soil, due to this property (Száková et al. 2009).

In the concentration correlation dendrogram of stream water, the As-concentrations are mostly related to the Fe-representing inducing element group, but less related to the Na, Mg, Ca representing cation exchange element group (Figure 9). This is similar to the relation of the As-concentrations with those of other elements in the groundwater of Bangladesh’s aquifer. The negative correlation between the As- and S- concentrations in the studied New Jersey
watershed (upstream correlation=-0.167, t= -1.49; downstream correlation =-0.68, t= -8.38, n=28) is likely due to S being mainly in its oxidized state of SO$_4^{2-}$ in the stream and an oxidizing environment which restricts the release of As. Two distinct groups in the concentration correlation dendrogram of lysimeter #1 can also be identified (Figure 10). Here the As-concentrations are closely related to the concentration group of Pb, Mn, Si, and Fe which is affiliated with a release by weathering processes under reducing conditions.

Arsenic in natural water occurs mainly as oxyanions in the form of trivalent arsenite (As(III)) and pentavalent arsenate (As(V)) with As(V) dominating (Smedley and Kinniburgh 2002). For the pH-ranges between 4.6 to 9.03 in the experiment leachates and 6.4 to 8.5 in groundwater and stream water, a generally oxidizing condition is present, so that HAsO$_4^{2-}$ and H$_2$AsO$_4^{-}$ are the main As-species based on previous studies (Smedley and Kinniburgh, 2002).

The negative correlation between the As- and Na- concentrations in both groundwater of the coastal aquifers from Bangladesh and the stream water in the New Jersey watershed (upstream correlation=- 0.23, t=2.02; downstream correlation= -4.1, t=4.03, n=28) is comparable to the corresponding correlation in the leachate from the NaCl only salt injection, when no As-minerals are added.

On the other hand, the positive correlation between As- and Fe- and As- and Mn-concentrations in all media implies that the release of As in groundwater and soil solution is more redox-controlled than salt-controlled (Figures 9, 10). Though the increased concentrations of divalent salt such as CaCl$_2$ and MgCl$_2$ can increase the release of As in the form of colloid adsorbents and dissolved HAsO$_4^{2-}$ and H$_2$AsO$_4^{-}$ species from the soil and coastal aquifer, the effect of a concentrated NaCl- solution on the release of As into groundwater and stream water is limited based on the results of our experimental and field data analyses.

6.2. Lead

In the regular soil-column experiments, hydrated Na$^+$-induced dispersion and Cl-complexation were at least partially responsible for the delayed increase of Pb-concentration in the leachate (Figure 3). Pb-concentrations measured in the leachate of arsenopyrite- and galena-added columns, even though higher than those in the leachate of regular soil columns, were significantly lower than the As-concentrations, due to the low solubility of PbS (Figure 4).
Because the divalent Ca\(^{2+}\) has a much stronger desorbing ability than the monovalent Na\(^+\), as discussed in the previous section (Meers et al. 2007; Menzies et al. 2007; Pueyo et al. 2004), the Pb-concentrations in the leachates of the mixed-salt experiments increased much more initially than in those of the single-salt experiments. In fact, the Pb-concentrations peaked in step with the Ca-concentration peak (Figure 5). Also, it is clear that the Pb concentrations are most closely correlated with those of S in the leachate of the mixed-salt experiments (Figure 10).

From the concentration-correlation dendrogram of the stream water of the New Jersey watershed (Figure 2), one may infer that the Pb-concentrations are most closely related to those of S (upstream correlation = 0.79, t=11.5; downstream correlation = 0.42, t=4.2, n=28), next closely related to those of Na and Cl (upstream correlations = 0.77 and 0.61, t=10.98 and 6.96, n=28; downstream correlation = 0.44, t=4.46, and 0.42, t=4.2, n=28) (Figure 9). This indicates that the Pb-concentration is at least partially controlled by an anthropogenic factor, because S-, Na-, and Cl- concentrations in stream water are all anthropogenically influenced (Rochelle et al. 1987; Sun et al. 2014). However, the Pb-concentrations are also positively correlated with those of Si in upstream water (correlation = 0.66, t=7.97, n=28) and in the soil solution from the lysimeter (correlation = 0.6, t=6.84, n=26), where the release of Si is related to the weathering process and so indicates a natural source of Pb (Figure 9).

Different from the natural release of Pb in ground water of coastal aquifers which originates mainly from the dissolution of Pb-oxide, carbonate, phosphate, sulfide, and sulfate minerals (Drever 1997), Pb in the stream water and soil solutions (Table 2) has a possible link to the anthropogenic input, likely the Pb-containing aerosol particles from the past use of Pb-additives in gasoline (Datko-Williams et al. 2014). Though Pb-emissions to air have decreased in the U.S. since the phase-out of Pb-containing gasoline in 1995, amounts of Pb in soils can still remain elevated for hundreds of years (Laidlaw et al. 2012; Datko-Williams et al. 2014). Atmospheric soil and Pb aerosols can also be re-suspended due to automotive traffic turbulence and deposited on the soil surface again, particularly, in the summer and fall, when the weather is dry (Laidlaw et al. 2012). Therefore, it is likely that the sources of Pb in the studied New Jersey watershed are a combination of natural and anthropogenic factors.
While the dissolution of various Pb-oxides, carbonate, phosphate, and sulfate minerals and desorption of various Pb-species absorbed onto organic matter, Fe and Mn oxyhydroxide, and clay particles in topsoil and coastal aquifers can result in diverse Pb-species such as Pb$^{2+}$, PbCO$_3$, PbCl$^-$, PbCl$_2$, PbCl$_3^-$, PbOH$^{2+}$, and Pb(CO$_3$)Cl$^-$ in ground- and surface water, as PbCl$_n$ makes up the majority of the Pb-species (Wei et al. 2005; Woosely and Millero 2012) in those water systems. Because increased Cl- concentrations will increase the amount of PbCl$_n$ in the solution, salt water intrusion from over-pumping and/or sea level rising in coastal regions and the application of deicing salt will likely increase the concentrations of Pb in the corresponding water system if an elevated source of Pb already exists.

6.3. Mercury

Sources of Hg in the leachates of soil column experiments are the soil minerals and the soil organic matter. Changes of the Hg-concentrations in the leachate, in response to the injection of a NaCl-solution, were similar to those of the Pb-concentrations and were facilitated by the dispersion-release and Cl-complexation (Figure 3).

There are significant positive correlations between the concentrations of Hg and those of Fe, Si, and Al. For the soil columns where arsenopyrite and galena were added, the release of Hg from the soil was similarly to that in the regular soil columns that have no minerals added (Figure 4). However, the Hg concentrations do not correlate with those of As and Pb, as it did in the regular soil columns, because of the enhanced As- and Pb-supplies in the mineral-added columns. For the injection of CaCl$_2$- and NaCl-mixed salt experiment, the changes of the Hg-concentrations in the leachate synchronized with those of Ca as well, similar to the behavior of other elements (Figure 5). Compared to the concentrations of other elements measured, the Hg-concentrations are generally lower in all the leachates, soil solutions, stream water and runoff water, probably due to the low stock of Hg in soils (Figures 3-7).

The Hg-concentrations in the stream water of the studied New Jersey watershed, even though low, are significantly correlated with those of Na, Cl, S, Mn, and Pb, only marginally correlated with those of Si (correlation=0.112, t=1.01, n=28), and almost have no correlation with Fe-concentrations (-0.01)(Figure 9). There are significant correlations between the Hg- and Na-concentrations (correlation=0.43, t=4.3, n=28) and Hg and S concentrations
A lack of significant correlation with Si indicates that the dominant source of Hg in the stream water is anthropogenic in this New Jersey watershed (Figure 2), similar to many other watersheds (Barringer et al. 2005; Tipping et al. 2011). The simulation study of Seigneur et al. (2004) indicates that anthropogenic emissions could constitute 80% of the Hg-deposition for the input of Hg in surface waters in northern New Jersey. This is different from the sources of Hg in the groundwater of the coastal aquifer in Italy, presented in Section 2.

Hg exists in water as Hg⁰, or Hg²⁺, and Hg₂²⁺ and has a strong tendency to form complexes with Cl⁻, OH⁻, S²⁻, and S⁻ containing functional groups of organic ligands, particularly, in a surface water body or shallow ground water. Cl forms hydroxide complexes with Hg²⁺ when the Cl²⁻ concentration is above 10⁻⁹ mol/l (Hahne and Kroontje 1973; Bollen et al. 2008). Bollen et al. (2008) found that 80% of their Hg exists as a reactive, inorganic Hg-species, such as HgCl₂ in both surface- and groundwater. Schuster (1991) stated that Cl may be regarded as one of the most mobile and persistent complexing agent for Hg. Since the solubilities of HgCl₂ and Hg(OH)₂ are rather high, the affinity of Hg to these ligands leads to an increased mobility of Hg. The relative high correlation between concentrations of Cl and Hg for stream water (correlation=0.55, t= 0.59, n=28) and in the samples of the saline ground water from Italy (correlation=0.88, t=7.78, n=18) (Section 2), both support the formation of HgCl₂ species in their water bodies. With an increased Cl-concentration in a water system, there will be an increased desorption of Hg from the soil mineral and the organic matter, and more Hg being mobilized from the coastal aquifer and the soil into groundwater and surface water. This indicates that exploitation of groundwater, the rising sea level along the coast and the increased application of road salt can all lead to increased interaction of Cl₂ with Hg in an aquifer and soil and may, consequently, increase the formation of HgClₙ complexes in groundwater and surface water.

**Conclusions**

Geochemistry data related with As, Pb, and Hg from coastal aquifers of Bangladesh and Italy, and soil solutions from a New Jersey watershed with winter deicing salt application, leachate from experiments of salt injections into soil columns were examined. In all water systems
where NaCl was the main influencing salt, As- concentrations in the water increased only under a reducing condition and, generally have a negative correlation with the chloride concentrations in the medium. However, concentrations of both Pb and Hg were positively correlated with those of Na and Cl measured in these waters, most likely, due to chloride complexation of Pb and Hg. In the mixed-salt injection experiment where CaCl$_2$ and NaCl were mixed at 6:4 weight ratio (as mandated by the state of Rhode Island’s deicing salt composition), the As-, Pb-, and Hg- concentrations all increased quickly after the salt injection. The quick release of all these three metals in the mixed-salt experiment might be due to the high desorption and cation-exchange capacity of the divalent cation Ca$^{2+}$. Salt water intrusion into a freshwater aquifer associated with increased coastal pumping activities and/or rising sea levels, will likely increase the salinity and the mobilization of Pb and Hg from the coastal aquifer, though the effect of sea salt on the release of As is limited. The increased release of Pb and Hg from soil by NaCl-deicing salt and the increased release of all three elements, As, Hg, and Pb, when a divalent cation is dominating in a salt will need to be considered when an environmental policy for selecting an appropriate deicing salt is rendered.

Acknowledgments
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References


Table 1. Correlation coefficients of As- and Cl- concentrations from coastal aquifers in Bangladesh

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<th>Mn and As</th>
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<td>t-test</td>
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*GBM Plain is the Ganges–Brahmaputra- Meghna river flood plain and only the As concentrations larger than 1.0 ppb in Helim et al. (2010) were used to avoid instrumental inaccuracy. t-0.05 is the t test critical value with 95% confidence level. An absolute t test value larger than the t-0.05 value indicates that the correlation coefficients are significant with 95% confidence.
Table 2. Elemental Concentrations of Runoff Water from two Sample Sites along a Transect of I-95*

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<tr>
<th>Sample</th>
<th>As</th>
<th>Pb</th>
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<th>Ca</th>
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<th>Mg</th>
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*L3C1 is the nearest sampling site to the edge of Interstate Highway 95. L3C3 is a sampling site that is 1.8 meters (6 feet) away from L3C1 and the edge of Highway 95.
Figure 1. Cl vs. Hg- concentrations from a coastal aquifer of Italy. Data are from Grassi and Netti (2000).
Figure 2. Location map of soil and water sampling sites in the studied Centennial Lake Watershed (CLW) at Lawrenceville, New Jersey
Figure 3. Changes of As, Pb, Hg, and Na- concentrations in the leachate for injection of NaCl into the regular soil column.
Figure 4. Changes of As, Pb, Hg, and Na- concentrations in leachate for injection of 0.25 moles NaCl into the arsenopyrite and galena mixed soil.
Figure 5. Changes of As, Pb, Hg, and Na- concentrations in the leachate for injection of 0.25 moles of mixed CaCl$_2$ and NaCl into the regular soil
Figure 6. Changes of As, Pb, Hg, and Na- concentrations from upstream sampling site between 2012 and 2013.
Figure 7. Changes of As, Pb, Hg, and Na- concentrations in soil solution collected by lysimeter #1 between 2012 and 2013.
Figure 8. Concentration correlation dendrogram for injection of 0.125 moles of NaCl into the regular soil column.
Figure 9. Concentration correlation dendrogram for water samples from the upstream site in the studied New Jersey watershed.
Figure 10. Concentration correlation dendrogram for soil solutions collected by lysimeter #1 in the studied New Jersey watershed.