



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

Hongbing Sun ^{a,*}, John Alexander ^a, Brita Gove ^a, Manfred Koch ^b

^a Department of Geological, Environmental, and Marine Sciences, Rider University, Lawrenceville, NJ, USA

^b Department of Geotechnology and Geohydraulics, University of Kassel, Kurt-Wolters Str. 34109 Kassel, Germany

ARTICLE INFO

Article history:

Received 11 March 2015

Received in revised form 16 July 2015

Accepted 17 July 2015

Available online 21 July 2015

Keywords:

Mobilization mechanism of As, Pb, and Hg

Groundwater sea water intrusion

Deicing salt

ABSTRACT

Water geochemistry data from complexly designed salt-solution injection experiments in the laboratory, coastal aquifers of Bangladesh and Italy, taken from the literature, and two salted watersheds of New Jersey, US were collected and analyzed to study the geochemical mechanisms that mobilize As, Pb, and Hg under varied salting conditions. Overall, increased NaCl-concentrations in aquifers and soil are found to increase the release of Pb and Hg into the water. Reducing environments and possible soil dispersion by hydrated Na⁺ 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 to the application of CaCl₂ 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. With the ongoing 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 help understand the complex relation between the concentrations of As, Pb, and Hg and increased salt level in a coastal aquifer and in soils of a salted watershed.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Arsenic (As), lead (Pb), and mercury (Hg) are three of the most concerned toxic metals in a water system. High As-concentrations in water can cause permanent damage to the ecosystem and are carcinogenic to people (Barringer et al., 2007; Smedley and Kinniburgh, 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).

With increased salt encroachment into the coastal aquifer due to the rising sea levels as well as groundwater over-pumping, and increased winter deicing salt applications in northern watersheds, many previous studies have expressed concerns with regard to the release of the overall prevalent trace metals Cd, Cu, Pb, Hg, and Zn to the supply of drinking water, owing to the elevated salt concentration in a coastal aquifer and growing use of deicing salt in watersheds in the northern US, Europe, and Canada (Grassi and Netti, 2000; Protano et al., 2000; Barringer et al., 2007; Amrhein et al., 1994; Amrhein and Strong, 1990; Backstrom et al., 2004; Bauske and Goetz, 1993; Kelly et al., 2008; Nelson et al., 2009; Norrström and Jacks, 1998). The causes of elevated trace metal concentrations, in response to the increased salt concentrations, have been attributed to cation exchange, and the presence of Cl and

* Corresponding author.

E-mail address: hsun@rider.edu (H. Sun).

organic complexes (Amrhein et al., 1994; Lumsdon et al., 1995; Nelson et al., 2009; Brady and Weil, 2008).

Previous studies generally separated the water quality change due to salt water intrusion and deicing salt application. Those studies largely focused on the concentration changes of Cd, Cu, Pb, and Zn in groundwater and soil solution in response to varied salt conditions (Backstrom et al., 2004; Menzies and Jacks, 1998; Nelson et al., 2009; Norrstrom and Jacks, 1998). There is an apparent lack of studies on the combined geochemical mechanisms that mobilize As, Pb, Hg, and other trace metals from a coastal aquifer and soils of a salted watershed.

The purpose of this study is to examine the aqueous geochemical conditions that mobilize As, Pb, and Hg from coastal aquifers and from soils in response to the seawater salt encroachment and deicing salt applications. Our examination will include analyses of geochemical data from the leachates of complexly designed column experiments, geochemical data from brackish groundwater of published articles, and of our own geochemical data from highway runoff, soil solutions, and stream water in two salted watersheds of New Jersey, US. Complexly designed column experiments compensate the regular NaCl-salt-only-scenario with a mixed CaCl₂- and NaCl-salting scenario as it is common in coastal aquifers and is increasingly common in inland regions of the northern hemisphere where deicing salt is applied. Arsenopyrite (FeAsS) and galena (PbS) minerals were added into two of the experimental soil columns to mimic an elevated source of As and Pb in an aquifer.

The results of this study will help to understand the geochemistry of As, Pb, and Hg release from coastal aquifers into groundwater and from salted watersheds to stream water. As such, the results of this study hopefully will provide further crucial evidence for recognizing the increased threat of As, Pb, and Hg to the health of a water system in a salting environment (Nelson et al., 2009; Rundgren et al., 1992; Tipping et al., 2010).

The paper is structured as follows. It will start with the presentation of the laboratory set-ups and the experimental results. Then it will proceed with the statistical analysis of the coastal-water-quality data of Bangladesh and Italy taken from the literature, followed by the presentation of our field methods applied to the analysis of runoff water samples, off the I-95 interstate, stream water from the Delaware river at Trenton, and soil solutions from lysimeters installed along the banks of the sampled stream sections. The paper concludes with a discussion on the mechanism of the As-, Pb-, and Hg-mobilizations under varied salting conditions in a natural water system as related to the data presented.

2. As, Pb, and Hg chemistry in the salt injection laboratory experiment

The salt injection batch experiment with regular and arsenopyrite and galena enhanced soil columns under controlled condition can help better understand the relations between concentrations of As, Pb, and Hg and varied salt environments.

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

NaCl is the most common salt in ground water in a coastal aquifer and the most common winter de-icing salt used in the northern hemisphere due to its effectiveness and low cost.

2.1.1. Experimental setup

Four columns with a diameter of 5.08 cm (2 in.) and height of 30.5 cm each were filled with about 480 g of loamy soil collected from A and upper B horizons near the upstream gage at the Centennial Lake Watershed (CLW), New Jersey (Fig. 1). The soils used in the four columns have an average porosity of 0.66, average hydraulic conductivity of 1.57 m/day, average pore volume of 298 cm³, and average organic matter content of 4.2% based on the loss on ignition (LOI) method.

Two of the four soil columns contained powdered arsenopyrite (~35 g) and galena (~70 g) mixture to initiate the potential elevated sources of As and Pb and to increase the reaction kinetics. The mineral powder layers were placed at about 1/5 from the bottom of the columns (at ~6 cm in a 30.5 cm high column). 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 mol of sodium chloride solutions (1100 ml in volume) were injected into each column, respectively. After the injection of the solution (pulsed injection) was complete, distilled water was added once or twice daily (an average of about 300 ml daily), with no overflow allowed. The flow velocity was roughly 0.52 m/day when the solution/water was added initially in all four columns. The velocity decreases as the hydraulic head drops.

The leachate of each soil column was collected for up to three weeks. Collection of the leachate ended 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 and in the background solution 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.

2.1.2. Results for injection into regular soil columns

For the injection of 0.125 mol 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 mol 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 (Fig. 2a).

The low numbers in the above concentration range are about the background concentrations of the corresponding element, before the salt injection, whereas 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 (Fig. 2b). 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. 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

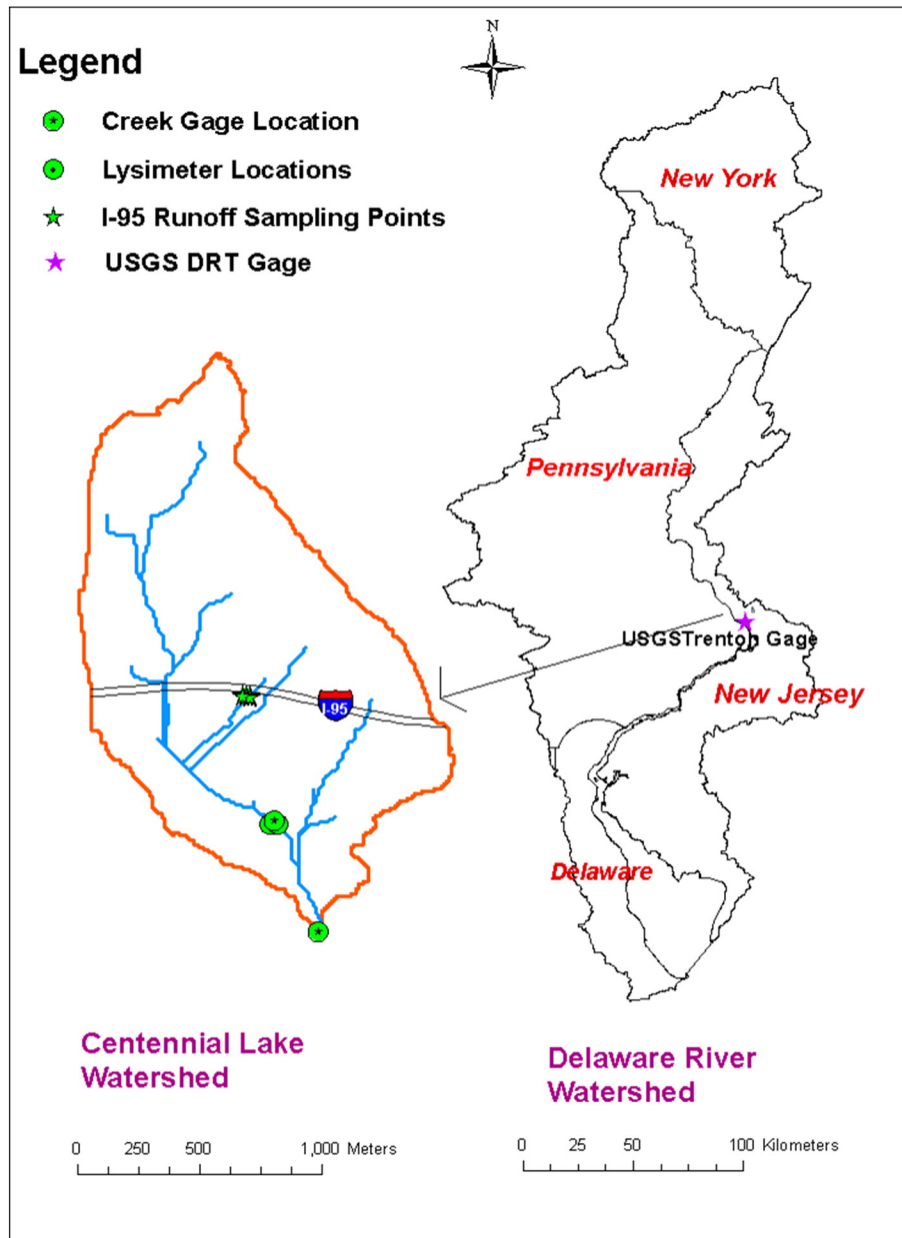


Fig. 1. Sample site location map of the studied watersheds. The Centennial Lake watershed (CLW, left) is located in the large Delaware River Watershed (right). DRT: Delaware River at Trenton station.

the concentration peaks of Na and Cl, which is likely due to the late release from dispersion of organic matter and clay minerals. The subsequent flushing of the soil columns with distilled water, following the injection of NaCl, leached soluble salts from the soil column and created a sodic soil condition in which soil aggregates and soil organic matter breaks up. This break-up of soil particles under sodic condition is called soil dispersion (deflocculation) (Brady and Weil, 2008). A sodic soil is a soil condition when its sodium ions are disproportionately high and the sodium adsorption ratio (SAR) is larger than 13 in its solution (Brady and Weil, 2008). Swarms of loosely

absorbed hydrated Na^+ surround the outer-sphere complexes of soil colloids and the poorly balanced electronegative colloids repel each other under such a sodic soil condition. These processes cause the soil particles to disperse, increase the reaction surface area, and accelerate the ion desorption and adsorption in a soil and an aquifer (Brady and Weil, 2008; Norrström and Bergstedt, 2001). The SAR values in the leachate were higher than 70 after the first day of the injection and were higher than 13 throughout the experiment time until the last day (Fig. 3). Therefore, the soil sodic condition exists throughout most of the run period of this NaCl injection experiment.

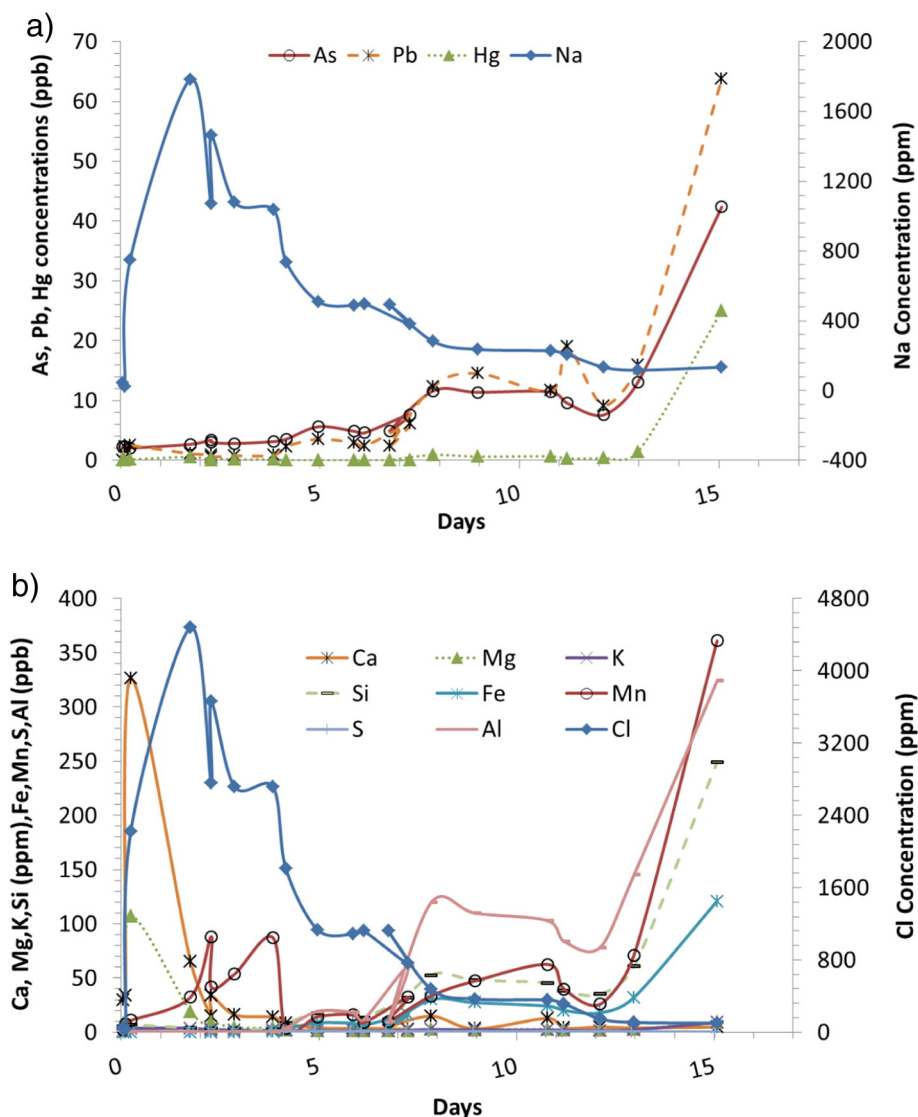


Fig. 2. a) Changes of As, Pb, Hg, and Na-concentrations, b) changes of Ca, Mg, K, S, Cl, Si, Al, Mn, P, and Fe, in the leachate of 0.25 mol of NaCl injection into the regular soil column. Note that in plot b), concentrations of Cl, Ca, Mg, K, and Si are in ppm while concentrations of Fe, S, Mn, and Al are in ppb.

2.1.3. Results for injection into arsenopyrite and galena mixed soil columns

For the injection of 0.125 mol of NaCl solution, the Na-concentrations in the leachate ranged from 33.3 to 1324.6 ppm (Fig. 4a) As- concentrations from 39.5 to 1621.7 ppb, and Pb-concentrations 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 (Fig. 4b). Hg-concentrations ranged from undetectable at the beginning of the experiment to 2.68 ppb near the end of the 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 soil dispersion. 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 (deflocculation) of organic matter under sodic soil condition due to high SAR values (Fig. 3), complexation with Cl, and an increased reducing environment after prolonged water flushing.

2.2. Injection of CaCl_2 and NaCl mixed salt into the regular soil column

CaCl_2 is a common sea salt in a salty coastal aquifer and the second most common deicing salt applied in the studied watersheds. Because mixed CaCl_2 and NaCl salts have been promoted as a more environmental friendly deicing combination and have gained popularity in recent years (Breault and

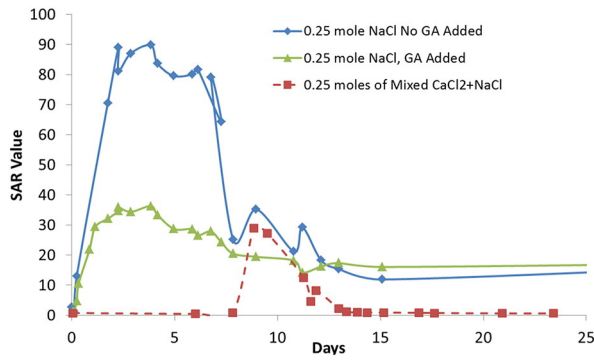


Fig. 3. Sodium adsorption ratios (SARs) for the three injection experiments shown in Figs. 2,4, and 5. Notice that the SAR value, which is an indication of the sodic soil condition for soil dispersion when it is larger than 13, were consistently high in the two 0.25 mol of NaCl injection experiments, while they only spiked for a short time in 0.25 mol of mixed CaCl₂ and NaCl injection experiment.

Smith, 2010), their effect on the mobilization of the As, Pb and Hg should be examined separately from that of regular NaCl salt alone.

2.2.1. Experimental setup

Soil column parameters (diameter, height, porosity, conductivity, flow rate, and pore volumes) are the same as those for the NaCl injection experiment of Section 2.1.2. However, here 0.25 and 0.5 molar solutions (1100 ml in volume) at a 6:4 weight ratio of CaCl₂:NaCl were injected into the two soil columns, respectively instead of NaCl only salt. The 6:4 CaCl₂:NaCl weight ratio was to mimic the salt mixing composition mandated since 1990 by the State of Rhode Island, USA, for its winter deicing road salt (Breault and Smith, 2010; Sun et al., 2012). The injections were followed by a daily flushing with about 300 ml of distilled water for three weeks, except weekends, similar to the injection of the NaCl experiment. The leachate of each soil column was collected at a

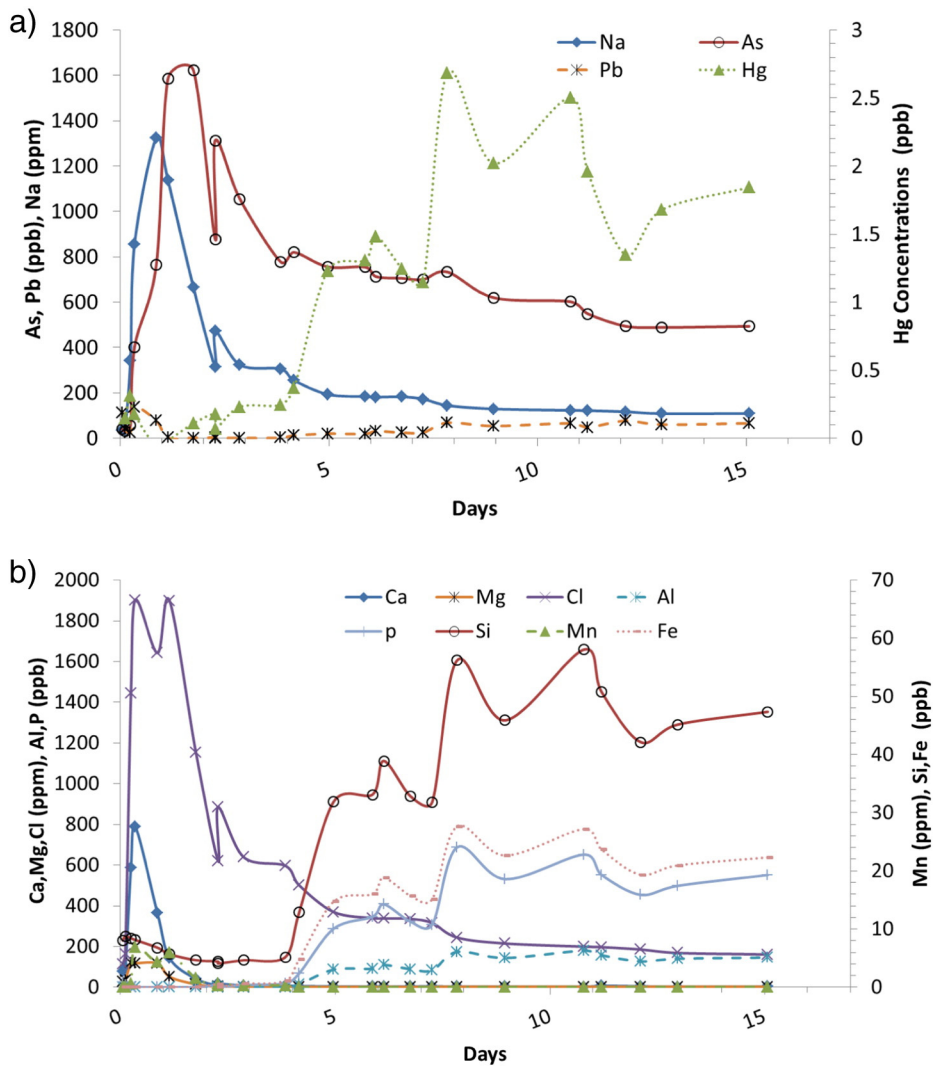


Fig. 4. a) Changes of As, Pb, Hg, and Na-concentrations, b) Changes of Ca, Mg, Cl, Si, Mn, Al P and Fe, in leachate of the injection experiment of 0.25 mol NaCl into the arsenopyrite and galena mixed soil.

regular interval during the injection period. Concentrations of the elements as listed in the following section were all measured by the ICP.

2.2.2. Results

Concentrations of all elements in the leachate from the injection of both the 0.25 and 0.5 mole solutions of mixed CaCl_2 and NaCl at the 6:4 ratio were always higher than those from the pure NaCl salt experiments discussed previously, and peaked almost in synchronization with that of Ca and Na (Fig. 5). This synchronization of the concentration change was due to the increased exchange capacity of Ca^{2+} , as it has already been verified in extraction studies of other metals (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 columns could be depleted by cation exchange, and because of much smaller SARs in these mixed salt injection, the delayed concentration increases of As, Pb, and Hg by the hydrated Na^+ induced soil dispersion were not as apparent as that in the pure NaCl injection experiment of the previous section.

For the injections of 0.25 and 0.5 mol 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 from 0.17 to 0.31 ppb and 0.45 to 3.45 ppb.

It is apparent from the results of these mixed salt injection experiments that increased salt concentrations also increase the release of metals, similar to the results from the single salt injection (Fig. 3). High concentrations of Mn and Fe in the leachate proved that CaCl_2 is also very effective in 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).

3. Release of As, Pb, and Hg in response to salinity changes in coastal aquifers

Arsenic (As) related geochemistry data from three areas: Gangers, Chapai-Nawabganj, and Meghna rivers across the country of Bangladesh were obtained from Reza et al. (2010a,b), Halim et al. (2010), and Shamsudduha et al. (2008). The delta area of Bangladesh where these data were collected is infamous for its high As-concentration in groundwater and As related health problems. The As-concentrations in some wells of the Chapai-Nawabganj district were as high as 462 ppb (Reza et al., 2010b).

Linear correlations between the concentrations of As and other elements based on those data were analyzed. Though the linear 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 the data and the conclusions presented by these researchers (Reza et al., 2010a,b; Halim et al., 2010) also indicate that the As-concentrations are generally positively correlated with that of a reducing environment indicator Mn.

A positive correlation between the As- and Mn-concentrations has also been reported 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.

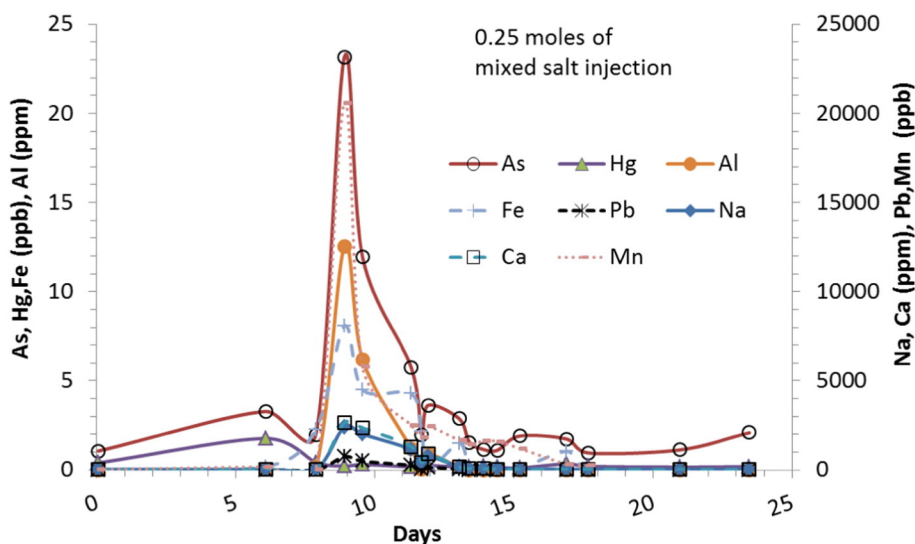


Fig. 5. Changes of As, Pb, Hg, and Na-concentrations in the leachate of the injection experiment of 0.25 mol of mixed CaCl_2 and NaCl into the regular soil column.

From the limited data analyzed in the Chapai Nawabganj region (Reza et al., 2010a), a positive correlation between the concentrations of Cl and Pb, though not statistically significant, was observed (Ganges Flood Plain, correlation = 0.06, $t = 0.14$, $n = 7$).

Here we also analyzed the geochemical data collected by Grassi and Netti (2000) for Ansedonia and Castiglione in the Pescaia region in Italy. Their data showed a clear relationship between concentrations of Hg and Cl (Fig. 6). The correlation coefficient between concentrations of Cl (salinity of 2 to 34) and Hg (0.5 to 5.5 $\mu\text{g/l}$) 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's (2000) study are also larger than 0.88.

4. As, Pb, and Hg chemistry in a watershed with large deicing salt application

4.1. Runoff water samples off an interstate highway

A total of nine runoff water sampling cups were buried right below the surface along three transects perpendicularly to Interstate highway 95 in the Centennial Lake Watershed (CLW), New Jersey, US, (Fig. 1). The three transects along I-95 are 0.9, 1.8, and 2.7 m behind the guardrail of the highway in a grassy area and are approximately 5 m apart. Five groups of samples were collected before and after salting periods between 2012 and 2013 (Table 2).

Overall, the peaked Na-concentration was more than 266 times (6678 ppm) those of the pre-salting Na-concentration (25.1 ppm) (Table 2). The SAR was as high as 237 on 2/13/2013 in transect 1 and was larger than 13 in all 18 samples collected in February 2013 (Table 2). This disproportional high Na-concentration created the field sodic soil condition and caused soil dispersion. Based on Sun et al. (2009, their Table 5), soil organic matter contents in the top soil at the studied I-95 transects ranged from 2.11% to 4.08% based on the loss on ignition (LOI) method. Therefore, dispersion of soil organic matter exists as well. The large surface area of the dispersed soil and soil organic colloids increases the reaction kinetics and so accelerates the adsorption and desorption processes.

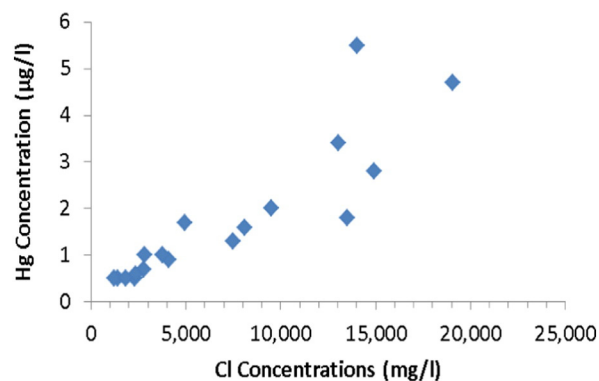


Fig. 6. Cl- versus Hg-concentrations from a coastal aquifer of Italy. Data are from Grassi and Netti (2000).

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 from undetectable to 4.4 ppb, with an average of 2.35 ppb, and Hg-concentrations were undetectable in all the samples. A possible association of the lowest As-concentrations with the highest Na-concentrations is the masking of the ICP sensitivity by the high intensity of Na, as discussed by Pueyo et al. (2004). The higher As-concentrations (on 2/27/2013 Table 2) obtained after the sodium peak had passed is likely due to the possible hydrated Na^+ induced dispersion of clay and organic matter under the sodic soil condition as discussed in Section 2.1.2 of the NaCl injection into a regular soil column. 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

Water geochemistry data for the Delaware River at Trenton (abbreviated as DRT from here in, Fig. 1), New Jersey were obtained from the USGS database between 2002 and 2015 when the As or Pb data were available. The water samples for the stream in the CLW, New Jersey were collected from two sample sites, one upstream and the other downstream, between 2011 and 2013.

The As-concentrations at the DRT gage station between 2008 and 2014 ranged from 1.8 to 0.19 ppb, and averaged 0.35 ppb whereas the Pb-concentration between 2003 and 2008 ranged from 0.06 to 0.63 ppb, with an average of 0.39 ppb for filtered data (unfiltered max concentration was 4.12 ppb). The upstream As-concentrations collected in our studied smaller CLW, during the 2012 to 2013 measuring period ranged from 0.28 to 2.35 ppb, and averaged to 1.08 ppb, with higher concentrations in the off-salting season (Fig. 7). Pb-concentrations ranged from 0.44 to 2.01 ppb, and averaged 0.95 ppb. Hg-concentrations ranged from undetectable to 2.0 ppb, and 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, from 0.48 to 1.1 ppb, with an average of 0.84 ppb for Pb, and from undetectable to 1.78 ppb, with an average of 0.47 ppb for Hg during the 2012 to 2013 measuring period. These results indicate that the concentration variation of the downstream water has the same pattern as that of the upstream water.

4.3. Soil solutions from lysimeters

Three suction soil lysimeters were buried at depths of approximately 110 cm from the surface along the banks of the upstream sample sites, with two lysimeters (#1 and #3) on one side of the bank and one lysimeter (#2) on the other side of the stream bank (Fig. 1). Lysimeters #1 and #2 are near the bank, and lysimeter #3 is approximately 7 m away from the bank.

Concentrations of most elements in the soil solutions collected by the lysimeters were significantly higher than those in the stream water of the CLW, except for that of Na and Cl (Fig. 8). 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

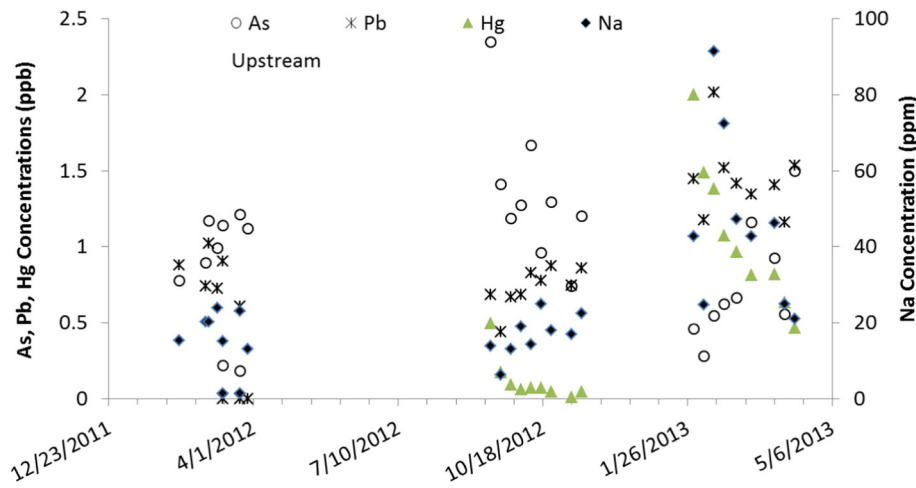


Fig. 7. Changes of As-, Pb-, Hg-, and Na-concentrations from the CLW upstream sampling site between 2012 and 2013.

average of 2.01 ppb and Hg-concentrations from undetectable to 2.55 ppb, with an average of 0.49 ppb. Because the lysimeters are located in the woods (Fig. 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 plotted with STATA program (Fig. 9). Correlation dendrogram shows how closely one cluster/group is correlated with another cluster/group. One group represents mainly the ion exchange elements Na, Cl, Mg, and Ca, whereas the other group represents the dispersion-weathering related elements: Fe, As, K, Mn, Si, P, Pb, and Hg. 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 Kinniburgh, 2002). The positive correlation between the concentrations of As and P implies a possible substitution of PO_4^{3-} and AsO_4^{3-} anionic groups in the minerals, because of their chemical similarity (Cornell and Schwertmann, 2003; Tessier et al., 1996). Such a positive relationship between concentrations of P and As was also reported in other studies (Smedley and Kinniburgh, 2002) and in a recent study for the DRT data by Sun et al. (2015).

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-

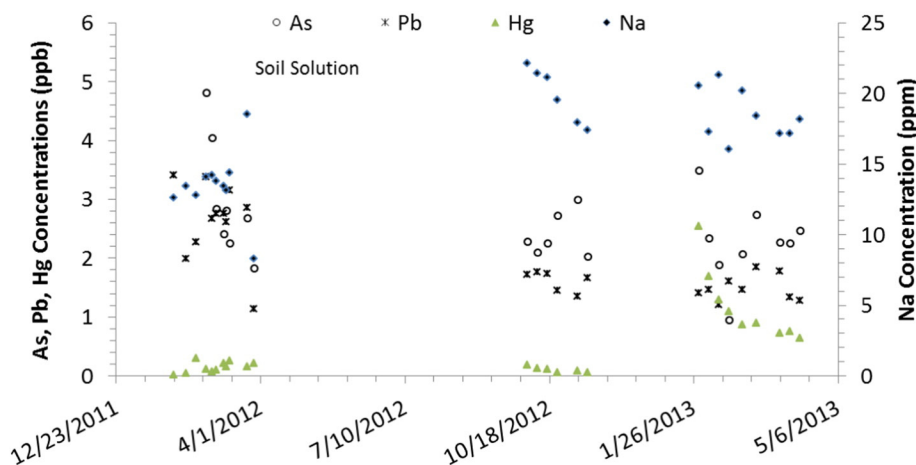


Fig. 8. Changes of As, Pb, Hg, and Na-concentrations in soil solution collected by lysimeter #1 from the CLW between 2012 and 2013.

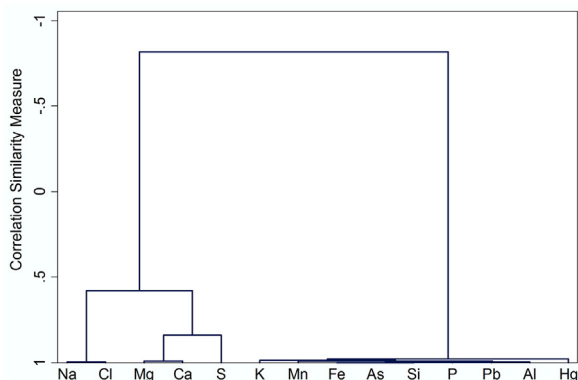


Fig. 9. Concentration correlation dendrogram for injection experiment of 0.125 mol of NaCl into the regular soil column.

concentrations in their leachates were in synchronization with the increases of Na-, Ca-, Mg-, and K-concentrations (Figs. 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 are formed by oxidation (Smedley and Kinniburgh, 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, due to this property, moderate to low concentrations of CaCl_2 have been used for that reason as a standard agent for extracting As from soil (Szaková 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 those of Na, Mg, Ca representing the ion exchange element group (Fig. 10). The correlations between the concentrations of As and Na, and As and Cl are also negative (Na and As correlation = -0.38 , $t = -2.36$, $n = 85$; Cl and As correlation = -0.41 , $t = -2.54$, $n = 85$). This is similar to the relation of the As-concentrations with those of other elements in the groundwater of Bangladesh's aquifer (Table 1). The negative correlation between the As- and S-concentrations in the studied New Jersey CLW 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 within an oxidizing environment which restricts the release of As. A negative correlation is also shown between the concentrations of As and SO_4^{2-} in the DRT, New Jersey (Correlation = -0.33 , $t = -2.97$, $n = 84$). Two distinct groups in the concentration correlation dendrogram of lysimeter #1 can also be identified (Fig. 11). 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

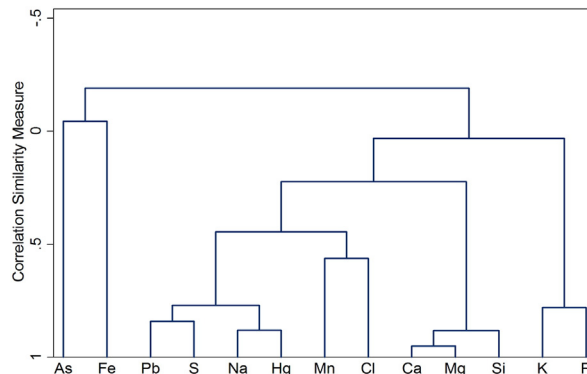


Fig. 10. Concentration correlation dendrogram for water samples from the CLW upstream site in the studied New Jersey watershed.

(As(V)) with As(V) dominating (Smedley and Kinniburgh, 2002) based on its pH-pe stability diagram (Fig. 12). The pe values for stream waters in Fig. 12 were estimated based on the measured temperature, pH, and DO values using PHREEQC (Parkhurst and Appelo, 1999). For the experiment leachates and the stream water, the pH ranges between 4.6 and 9.03, and a generally oxidizing condition is present, hence, HAsO_4^- and H_2AsO_4^- are the main As-species.

The negative correlations between the As- and Na-concentrations in both groundwater of the coastal aquifers from Bangladesh (Table 1) and the stream water in the New Jersey watersheds (CLW upstream correlation = -0.23 , $t = -2.02$; CLW downstream correlation = -4.1 , $t = 4.03$, $n = 28$, DRT correlation = 0.37 , $t = -3.75$, $n = 85$) are comparable to the corresponding correlation in the leachate from the NaCl only salt injection, when no As-minerals are added (correlation = -0.401 , $t = -2.1$, $n = 25$).

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 (Figs. 10, 11). Though the increased concentrations of divalent salt such as CaCl_2 and MgCl_2 , and soil dispersion under sodic condition can increase the release of As in the form of colloid adsorbents and dissolved HAsO_4^- and H_2AsO_4^- species (Fig. 12), a positive correlation between the concentrations of NaCl and As in groundwater and stream water cannot be corroborated based on our laboratory and field data.

5.2. Lead

In the regular soil-column experiments, hydrated Na^+ -induced soil dispersion under sodic soil condition and Cl-complexation were at least partially responsible for the delayed increase of Pb in the leachate (Fig. 2). 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 (Fig. 4). Because the divalent Ca^{2+} has a much stronger desorbing ability than the monovalent Na^+ , as discussed in the previous section and other studies (Meers et al., 2007; Menzies et al., 2007; Pueyo et al., 2004), the Pb-concentrations in the leachates of the

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

	Cl and As		Mn and As		Shared parameters			Sources
	Corr. coeff	t-test	Corr. coeff	t-test	t-0.05	Sample size	Well depth (m)	
GBM Plain ^a	-0.11	-0.22	0.19	1.07	2.04	33	266.7	Halim et al. (2010)
Manikganj flood plain	-0.34	-1.03	0.08	0.35	2.26	10	103.2	Reza et al., (2010a)
Meghna	-0.71	-3.16	-0.56	-1.64	2.23	11	160.6	Reza et al., (2010a)
Chapai-Nawabganj	0.02	0.08	0.24	1.09	2.09	20	82.7	Reza et al., (2010a)
Chapai-Nawabganj	-0.31	-1.44	0.4	1.73	2.09	20	51.9	Reza et al., (2010b)
Ganges-Brahmaputra	-0.16	-1.45	-0.54	0.11	1.99	84	51.9	Shamsudduha et al. (2008)

^a 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.

mixed-salt experiments increased much more than in the single-salt experiments initially. In fact, the Pb-concentrations peaked in step with the Ca-concentration peak (Fig. 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.

From the concentration-correlation dendrogram of the CLW stream water of the New Jersey watershed (Fig. 10), one may infer that the Pb-concentrations are most closely related to those of S (CLW upstream correlation = 0.79, $t = 11.5$; CLW downstream correlation = 0.42, $t = 4.2$, $n = 28$), next closely related to those of Na and Cl (CLW upstream correlations = 0.77 and 0.61, $t = 10.98$ and 6.96, $n = 28$; CLW downstream correlation = 0.44, $t = 4.46$, and 0.42, $t = 4.2$, $n = 28$) (Fig. 10). The positive correlation between Pb- and Cl-concentrations was also observed for the water data measured by the USGS from the large DRT watershed in New Jersey between 2002 and 2008 when the Pb was measured more frequent (correlation = 0.32, $t = 1.6$, $n = 25$, Fig. 13). 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). In addition, the Pb-concentrations are also positively correlated with those of Si in the CLW 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 (Fig. 11).

Different from the natural release of Pb in ground water of coastal aquifers which originates mainly from the dissolution of

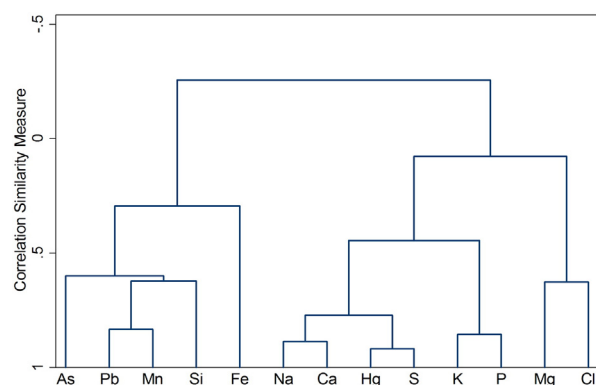


Fig. 11. Concentration correlation dendrogram for soil solutions collected by lysimeter #1 in the studied CLW watershed.

Pb-oxide, carbonate, phosphate, sulfide, and sulfate minerals (Drever, 1997), Pb in the stream water and in the soil solutions (Table 2) has a possible anthropogenic source, such as, likely, the Pb-containing aerosol particles from the past use of Pb-additives in gasoline (Datko-Williams et al., 2014; Harrison et al., 1981; Sarwar et al., 2015). 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; Sarwar et al., 2015). 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 most likely that the sources of Pb in the studied New Jersey watersheds are a combination of natural and anthropogenic factors.

The dissolution of various Pb-oxides, carbonate, phosphate, and sulfate minerals and the desorption of various Pb-species adsorbed onto organic matter, Fe and Mn oxyhydroxide, and on 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 waters (Wei et al., 2005; Woosley and Millero, 2013) (Fig. 12). Because salt water intrusion accelerated by over-pumping and/or sea level rising

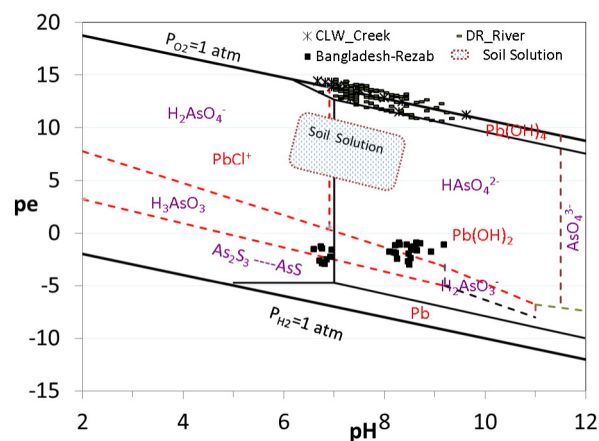


Fig. 12. Simplified PHREEQC-generated pe–pH diagram for the system of As–O–S–H₂O (dash boundary lines) and Pb–Cl–OH (solid boundary lines) at 25 °C and one atmospheric pressure for the estimated pe–pH data from the stream water of DRT gage station, the creek water and soil solution in CLW, and groundwater data from Bangladesh of Reza et al. (2010b).

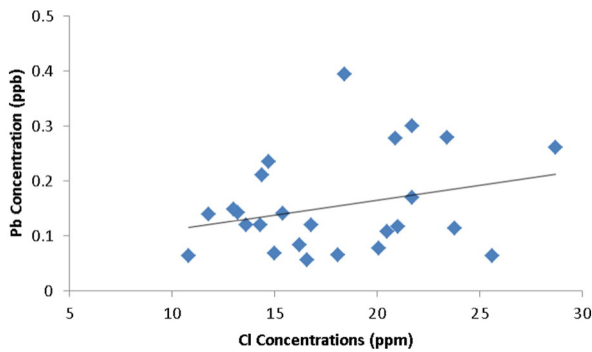


Fig. 13. Pb and Cl concentrations measured at the DRT gage station between 2002 and 2008 with a trend line added. Data were obtained from USGS database.

in coastal regions and the application of deicing salt will likely increase the Cl-concentrations, the amount of $PbCl_n$ and other dissolved Pb species related to the salt also will increase in the groundwater of a salty coastal aquifer and soil solution of a salted watershed (Fig. 13).

5.3. Mercury

Sources of Hg in the leachates of the 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 pure NaCl-solution, were similar to those of the Pb-concentrations and were facilitated by the soil dispersion and Cl-complexation (Figs. 2, 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 (Fig. 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 mixed $CaCl_2$ - and NaCl-injection experiments, the changes of the Hg-concentrations in the leachate synchronized with those of Ca as well, similar to the behavior of other elements (Fig. 5).

Compared to the concentrations of other elements measured, the Hg-concentrations are generally lower in all the leachates, soil solutions, stream water and the runoff water (Figs. 2–7).

The Hg-concentrations in the stream water of the studied CLW 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 (upstream correlation = 0.112, $t = 1.01$, $n = 28$), and almost have no correlation with Fe-concentrations (-0.01) (Fig. 10). There are significant correlations between the Hg- and Na-concentrations (upstream correlation = 0.66, $t = 3.56$, $n = 18$; downstream correlation = 0.43, $t = 2.34$, $n = 28$) and the Hg- and S-concentrations (upstream correlation = 0.67, $t = 3.59$, $n = 18$; downstream correlation = 0.86, $t = 5.7$, $n = 28$) in the water of the CLW watershed as well. A lack of significant correlation with Si, on the other hand, indicates that the dominant source of Hg in the stream water is anthropogenic in this New Jersey watershed (Fig. 1), similar to many other watersheds (Barringer et al., 2005; Tipping et al., 2010). 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 3 (Fig. 6).

Hg exists in water as Hg^0 , or Hg^{2+} , and Hg_2^{2+} and has a strong tendency to form complexes with Cl^- , OH^- , S^{2-} , and S^- containing functional groups of organic ligands, particularly, in a surface water body or shallow ground water as seen in the pe-pH diagram of Hg-Cl-S- H_2O (Fig. 14). Cl forms hydroxide complexes with Hg^{2+} when the Cl^{2-} concentration is above 10^{-9} mol/l (Hahne and Kroontje, 1973; Bollen et al., 2008). Bollen et al. (2008) found that 80% of the Hg in their soil and groundwater samples exists as a reactive, inorganic Hg-species, such as $HgCl_2$. Schuster (1991) stated that Cl may be regarded as one of the most mobile and persistent complexing agent for Hg. Since the solubilities of $HgCl_2$ 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 both the CLW stream water (upper stream correlation = 0.55, $t = 3.23$, $n = 26$) and in the samples of the saline ground water from Italy (correlation = 0.88, $t = 7.78$, $n = 18$) (Section 3), supports the formation of

Table 2
Elemental concentrations of runoff water from two sample sites along a transect of I-95^a.

Sample	ppb As	ppb Pb	ppm Na	ppm Ca	ppm K	ppm Mg	ppb Mn	ppm Fe	ppm Al	ppb P	ppm S	ppm Cl	SAR
L3C1													
11/7/2012	1.16	2.50	25.3	21.03	3.66	6.67	–	5.18	0.31	1.03	0.18	11.5	1.7
11/14/2012	1.05	2.17	1185.7	212.30	22.34	89.31	–	0.13	0.31	0.30	2.24	4471.6	24.3
2/6/2013	2.59	2.83	2095.3	116.53	11.27	32.66	0.52	0.00	0.31	0.17	3.46	6469.6	62.4
2/12/2013	0.83	3.06	6678.0	237.84	27.21	60.44	2.10	–	0.31	0.95	16.62	12,762.6	141.2
2/27/2013	3.14	3.56	2765.2	71.10	9.68	13.33	2.86	0.02	0.31	7.52	4.53	9376.9	111.4
L3C3													
11/7/2012	1.65	1.71	31.7	3.21	5.90	1.06	1.08	66.00	0.40	19.81	0.20	11.3	5.5
11/14/2012	1.03	2.45	896.3	76.64	21.52	30.84	59.86	3.04	0.31	2.78	1.31	3048.0	30.8
2/6/2013	2.82	3.23	908.6	45.18	7.88	10.77	39.14	0.01	0.31	2.84	1.07	2751.7	44.5
2/12/2013	0.83	2.34	5196.5	169.91	19.80	32.52	61.89	–	0.31	1.44	10.44	12,419.9	135.1
2/27/2013	2.65	3.54	1350.2	45.62	9.21	9.33	5.74	0.04	0.30	2.60	1.45	4847.6	67.2

^a L3C1 is the nearest sampling site to the edge of Interstate Highway 95. L3C3 is a sampling site that is 1.8 m (6 ft) away from L3C1 and the edge of Highway 95.

HgCl₂ species in these 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 ongoing exploitation of groundwater, the rising sea level along the coast and the increased application of road salt can all lead to an increased interaction of Cl with Hg in an aquifer and soil and may, consequently, increase the formation of HgCl_n complexes in groundwater and surface water.

6. Conclusions

Geochemistry data related to As, Pb, and Hg from the leachate of salt injection experiments, groundwater of coastal aquifers of Bangladesh and Italy, and stream water and soil solutions from two watersheds in New Jersey, US, with winter deicing salt application, 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, which, most likely, is due to chloride complexation of Pb and Hg and soil dispersion related desorption under a sodic soil condition.

In the mixed-salt injection experiment where CaCl₂ and NaCl were mixed at a 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 which may be due to the high desorption and cation-exchange capacity of the divalent cation Ca²⁺.

Salt water intrusion into a freshwater aquifer associated with increased coastal pumping activities and/or rising sea levels, will likely also 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 the 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

The authors thank Nicholas Mazza, Eric Pezzi, Nicole Chakowski, Leeann Sinpatanasakul, Maria Huffine, and Jonathan Husch from the Department of Geological, Environmental, and Marine Sciences (GEMS) at Rider University for their field and laboratory assistance during this project. We also acknowledge the critical comments of Kathy Brown from Rider University which improved the paper significantly. Finally, we acknowledge the financial support of Rider University and US National Science Foundation grant MRI-0821172.

References

- Amrhein, C., Strong, J.E., 1990. The effect of deicing salts on trace metal mobility in roadside soils. *J. Environ. Qual.* 19, 765–772.
- Amrhein, C., Mosher, P.A., Strong, J.E., Pacheco, P.G., 1994. Heavy metals in the environment, trace metal solubility in soils and waters receiving deicing salts. *J. Environ. Qual.* 23, 219–227.
- Backstrom, M., Karlsson, S., Backman, L., Folkesson, L., Lind, B., 2004. Mobilization of heavy metals by deicing salts in a roadside environment. *Water Res.* 38, 720–732.
- Barringer, J.L., Szabo, Z., Kauffman, L.J., Barringer, T.H., Stackelberg, P.E., Ivahnenko, T., Rajagopalan, S., Krabbenhoft, D.P., 2005. Mercury concentrations in water from an unconfined aquifer system, New Jersey coastal plain. *Sci. Total Environ.* 346, 169–183.
- Barringer, J.J., Bonin, J.L., Deluca, M.J., Romagna, T., Cenzo, K., Alebus, M., Kratzer, T., Hirst, B., 2007. Sources and temporal dynamics of arsenic in a New Jersey watershed, USA. *Sci. Total Environ.* 379, 56–74.
- Bauske, B., Goetz, D., 1993. Effects of deicing-salts on heavy metal mobility. *Acta Hydrochim. Hydrobiol.* 21, 38–42.
- Bollen, A., Wenke, A., Biester, H., 2008. Mercury speciation analyses in HgCl₂-contaminated soils and groundwater—implications for risk assessment and remediation strategies. *Water Res.* 42, 91–100.
- Brady, N.C., Weil, R.R., 2008. *The Nature and Properties of Soils*. 14th Ed Prentice Hall, New Jersey.
- Breault, R.F., Smith, K.P., 2010. Streamflow, water quality, and constituent loads and yields, scituate reservoir drainage Area, Rhode Island, Water Year 2009. USGS Open-File Report 2010–1275.
- Cornell, R.M., Schwertmann, U., 2003. *The Iron Oxides – Structure Properties, Reactions, Occurrences and Uses*. VCH Publishers, Weinheim.
- Datko-Williams, L., Wilkie, A., Richmond-Bryant, J., 2014. Analysis of U.S. soil lead (Pb) studies from 1970 to 2012. *Sci. Total Environ.* 468–469, 854–863.
- Drever, J.I., 1997. *The Geochemistry of Natural Waters*. 3rd Ed. Prentice Hall, New Jersey.
- Grassi, S., Netti, R., 2000. Sea water intrusion and mercury pollution of some coastal aquifers in the province of Grosseto (Southern Tuscany – Italy). *J. Hydrol.* 237, 198–211.
- Hahne, H.C.H., Kroontje, W., 1973. Significance of pH and chloride concentration on behavior of heavy metal pollutants: mercury(II), cadmium(II), zinc(II), and lead(II). *J. Environ. Qual.* 2, 444–450.
- Halim, M.A., Majumder, R.K., Nessa, S.A., Hiroshiro, Y., Sasaki, K., Saha, B.B., Saepuloh, A., Jinno, K., 2010. Evaluation of processes controlling the geochemical constituents in deep groundwater in Bangladesh. *J. Hazard. Mater.* 180, 50–62.
- Harrison, R.M., Laxen, D.P., Wilson, S.J., 1981. Chemical associations of lead, cadmium, copper, and zinc in street dusts and roadside soils. *Environ. Sci. Technol.* 15, 1378–1383.
- Kelly, V.R., Lovett, G.M., Weathers, K.C., Findlay, S.E.G., Strayer, D.L., Burns, D.J., Likens, G.E., 2008. Long-term sodium chloride retention in a rural watershed: legacy effects of road salt on streamwater concentration. *Environ. Sci. Technol.* 42, 410–415.
- Laidlaw, M.A.S., Zahran, S., Mielke, H.W., Taylor, M.P., Filippelli, G.M., 2012. Resuspension of lead contaminated urban soil as a dominant source of atmospheric lead in Birmingham, Chicago, Detroit and Pittsburgh, USA. *Atmos. Environ.* 49, 302–310.
- Lumsdon, D.G., Evans, L.J., Bolton, K.A., 1995. The influence of pH and chloride on the retention of cadmium, lead, mercury and zinc by soils. *J. Soil Contam.* 4, 137–150.

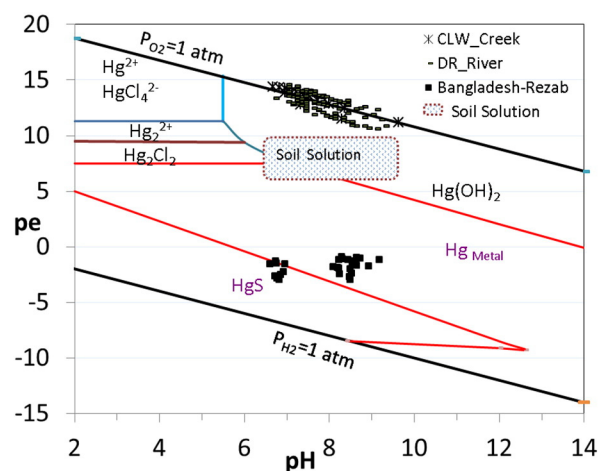


Fig. 14. Simplified PHREEQC-generated pe–pH diagram for the system of Hg–Cl–S–H₂O at 25 °C and one atmospheric pressure for the estimated pe–pH data from the stream water of DRT, the creek water and soil solution in the CLW, and groundwater data of Bangladesh of Reza et al. (2010b).

- Meers, E., Samson, R., Tack, F.M.G., Ruttens, A., Vandegheuchte, M., Vangronsveld, J., Verloo, M.G., 2007. Phytoavailability assessment of heavy metals in soils by single extractions and accumulation by *Phaseolus vulgaris*. *Environ. Exp. Bot.* 60, 385–396.
- Menzies, A.C., Jacks, G.S., 1998. Concentration and fractionation of heavy metals in roadside soils receiving de-icing salts. *Sci. Total Environ.* 218, 161–174.
- Menzies, N.W., Donn, M.J., Kopittke, P.M., 2007. Evaluation of extractants for estimation of the phytoavailable trace metals in soils. *Environ. Pollut.* 145, 121–130.
- Nelson, S., Yonge, D., Barber, M., 2009. Effects of road salts on heavy metal mobility in two eastern Washington soils. *J. Environ. Eng.* 135, 505–510.
- Norrström, A.C., Bergstedt, E., 2001. The impact of road de-icing salts (NaCl) on colloid dispersion and base cation pools in roadside soils. *Water Air Soil Pollut.* 127, 281–299.
- Norrström, A.C., Jacks, G., 1998. Concentration and fractionation of heavy metals in roadside soils receiving de-icing salts. *Sci. Total Environ.* 218, 161–174.
- Parkhurst, David L., Appelo, C.A.J., 1999. User's guide to PHREEQC (Version 2): a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. Open-File Reports Section, Water-Resources Investigations Report 99-4259 xiv. U.S. Geological Survey: Earth Science Information Center, p. 312.
- Protano, G., Riccobono, F., Sabatini, G., 2000. Does salt water intrusion constitute a mercury contamination risk for coastal fresh water aquifers? *Environ. Pollut.* 110, 451–458.
- Pueyo, M., López-Sánchez, J.F., Rauret, G., 2004. Assessment of CaCl₂, NaNO₃ and NH₄NO₃ extraction procedures for the study of Cd, Cu, Pb and Zn extractability in contaminated soils. *Anal. Chim. Acta* 504, 217–226.
- Reza, S.A.H.M., Jean, J.S., Lee, M.-K., Liu, C., Bundschuh, J., Yang, H., Lee, J., Lee, Y.C., 2010a. Implications of organic matter on arsenic mobilization into groundwater. *Water Res.* 44, 5556–5574.
- Reza, S.A.H.M., Jean, J.S., Yang, H., Lee, M.-K., Woodall, B., Liu, C., Lee, J., Luo, S., 2010b. Occurrence of arsenic in core sediments and groundwater in the Chapai-Nawabganj District, northwestern Bangladesh. *Water Res.* 44, 2021–2037.
- Rochelle, B.P., Church, M.R., David, M.R., 1987. Sulfur retention at intensively studied sites in the U.S. and Canada. *Water Air Soil Pollut.* 33, 73–83.
- Rundgren, S., Ruhling, A., Schluter, K., Tyler, G., 1992. Mercury in soil—distribution, speciation and biological effects. A Review of the Literature and Comments on Critical Concentrations. Nordic Council of Ministers, Copenhagen.
- Sarwar, M., Panuccio, E., Schwartz, S., Sun, H., 2015. Lead concentrations in soil profiles of a transect near an interstate highway in New Jersey. *Geol. Soc. Am. Vol. 47* (3), 71 (Abstracts with Programs).
- Schuster, E., 1991. The behaviour of mercury in the soil with special emphasis on complexation and adsorption processes—a review of the literature. *Water Air Soil Pollut.* 56, 667–680.
- Seigneur, C., Vijayaraghavan, K., Lohman, K., Karamchandani, P., Scott, C., 2004. Global source attribution for mercury deposition in the United States. *Environ. Sci. Technol.* 38, 555–569.
- Shamsudduha, M., Uddin, A., Saunders, J.A., Lee, M.-K., 2008. Quaternary stratigraphy, sediment characteristics and geochemistry of arsenic-contaminated alluvial aquifers in the Ganges–Brahmaputra floodplain in central Bangladesh. *J. Contam. Hydrol.* 99, 112–136.
- Smedley, P.L., Kinniburgh, D.G., 2002. A review of the source, behavior and distribution of arsenic in natural waters. *Appl. Geochem.* 17, 517–568.
- Sun, H., Nelson, M., Chen, F., Husch, J., 2009. Soil mineral structural water loss during LOI analyses. *Can. J. Soil Sci.* 89, 603–610.
- Sun, H., Sinpatanasakul, L., Husch, J.M., Huffine, M., 2012. Na/Cl molar ratio changes during a salting cycle and its application to the estimation of sodium retention in salted watersheds. *J. Contam. Hydrol.* 136–137, 96–105.
- Sun, H., Alexander, J., Gove, B., Pezzi, E., Chakowski, N., Husch, J., 2014. Mineralogical and anthropogenic controls of stream water chemistry in salted watersheds. *Appl. Geochem.* 48, 141–154.
- Sun, H., Barton, A., Sarwar, M., Panuccio, E., 2015. Role of phosphate in the mobilization of arsenic from soil and aquifer. *Geol. Soc. Am. Abstr. Programs Vol. 47* (3), 72 (<https://gsa.confex.com/gsa/2015NE/webprogram/Paper252310.html>).
- Szákóvá, J., Tlustos, P., Goessler, W., Frková, Z., Najmanová, J., 2009. Mobility of arsenic and its compounds in soil and soil solution: the effect of soil pretreatment and extraction methods. *J. Hazard. Mater.* 172, 1244–1251.
- Tessier, A., Campbell, P.G.C., Bisson, M., 1979. Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.* 51, 844–851.
- Tessier, A., Fortin, D., Belzile, N., DeVitre, R.R., Leppard, G.G., 1996. Metal sorption to diagenetic iron and manganese oxyhydroxides and associated organic matter: narrowing the gap between field and laboratory measurements. *Geochim. Cosmochim. Acta* 60, 387–404.
- Tipping, E., Lofts, S., Hooper, H., Frey, B., Spurgeon, D., Svendsen, C., 2010. Critical limits for Hg(II) in soils, derived from chronic toxicity data. *Environ. Pollut.* 158, 2465–2471.
- Wei, Y.L., Yang, Y.W., Lee, J.F., 2005. Lead speciation in 0.1 N HCl-extracted residue of analog of Pb-contaminated soil. *J. Electron Spectrosc. Relat. Phenom.* 144–147, 299–301.
- Woosley, R.J., Millero, F.J., 2013. Pitzer model for the speciation of lead chloride and carbonate complexes in natural waters. *Mar. Chem.* 149, 1–7.