Source analysis of heavy metals in topsoil and water in arid area: a case study in northwest China

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Abstract. To understand the origin of metals in the topsoil, surface and ground water in arid area, field investigation and statistics were used in a chromium contaminated site in northwest China. The strong positive correlations among the soil EC, salinity and pH are attributed to the extensive evaporation and leaching of the chromite, lignite, limestone and dolomite. The scarce precipitation is responsible for the accumulation of metals in the topsoil. The soil salinization influences the metal mobility. Cr, Fe, Ni, As, Hg, V and Sb in the topsoil correlate with the chromite and lignite. Se, Cu, Co and Zn are mainly from geologic origin. The increase of As, Cr, Fe, Hg and Ni in the artificial channel reveals the influence of the soil leaching and groundwater discharge. The high content of Ca\textsuperscript{2+}, Mg\textsuperscript{2+}, Cl\textsuperscript{-}, SO\textsubscript{4}\textsuperscript{2-} and HCO\textsubscript{3}\textsuperscript{-} in the groundwater is resulted from the arid climate, artificial channel, limestone, dolomite and lignite. Cr, Fe, Ni and Hg in the groundwater primarily derive from the chromite and lignite, and Cd, Mn and Pb may be from the strata. Therefore, the factory synchronously makes the soil metals, EC, salinity and pH increase, and the salinization conversely influences the fate and transport of the metals.

1. Introduction
The metal contamination is a global issue, and is harming food safety, ecological and human health [1-2]. The fate and transport of metals are influenced by many factors, including precipitation, evaporation, and the physiochemical properties of environmental media[3-4]. In arid area, scarce precipitation and strong evaporation cause the fate and transport of metals to be complex, which make it difficult to identify the origin of metals and the factors influencing metal behaviors. A chromium contaminated site in arid area in northwest China, characterized by high electrical conductivity (EC), salinity and pH, and heavy metal contamination, may be employed to help to understand the metal fate and transport. In the soil and water in such a chromium contaminated site, besides the geologic origin, metals may derive from the production process. Use of limestone, dolomite and soda in the production process, and salinization due to the extremely small precipitation and extensive evaporation increase...
the electrical conductivity (EC), salinity and pH of the soil and water, and then may pose considerable effects on the metal mobility[5-6].

The equilibriums of metals between soil solid and water are controlled by soil properties, metal chemistry, and environmental factors[7-8]. In arid area, soils, especially the topsoil, and water are usually characterized by high concentration of salt ions and pH[9], which implies that salinity (or EC) and pH may play an important role in metal mobility and release in the soil and water. K⁺, Na⁺, Ca²⁺, Mg²⁺, Cl⁻, SO₄²⁻, HCO₃⁻, and PO₄³⁻ are primary ions in soil and water, which have significant influences on metal retention on soil solid and in soil solution[10]. Under alkaline and oxidation conditions, soils generally become more negatively charged, and Cr, As, Se, Sb and V usually exist as oxyanions [11-12]. K⁺, Na⁺, Ca²⁺ and Mg²⁺ are prone to sorption on soil surface, whereas, Cr, As, Se, Sb and V retain in solution, or partly adsorb on soil particles through the cation bridge[13], where anions such as PO₄³⁻, SO₄²⁻, HCO₃⁻ compete adsorption sites[14]. Cu, Co, Ni, Pb, Zn, Hg and Cd often exist in form of cation in this Eh-pH condition[15], and the negative charged surface is favorable for them retaining on the soil solid. But this process will be influenced by K⁺, Na⁺, Ca²⁺ and Mg²⁺. Under alkaline and reduction condition, except for Co and Zn, the variable valence metals will be reduced and dominated in form of low valence or Cr(OH)₃, H₂AsO₃⁻, SeO₃²⁻, Sb(OH)₃, CdS, Hg₂S and CuS [16]. Besides, reduction and dissolution of iron and manganese oxides have a direct impact on the adsorptive capacity of soils. In arid area, evaporation and periodical precipitation can break the soil equilibrium through changing soil Eh, pH, and content of cations and anions in the soil solution, hence, mobility and release of metals [17-18].

Simultaneous occurrences of metals in strata, hence, in soils can be explained by their geochemical classification and substitution. The siderophilic elements are those primarily associated with the iron-nickel core of the earth, including Fe, Ni, Co and Pt[19]. The chalophilic elements are associated with reduction environments and hydrothermal conditions, including Cu, Pb, Zn, Hg, Cd and As[20]. The lithophilic elements are common elements in crustal silicates, such as K, Na, Ca, Mg, Ba, and Al. Therefore, there are some correlation among metals, salinity and pH, which will make it possible to discuss the metal origin in a contaminated site in arid area. The study case is a factory producing dichromate with lime-based roasting method in arid region, and chromite ores, lignite, limestone, dolomite, soda, and sulfuric acid are the main materials. Salinity and pH of the soil and water, derived from the pollution sources and the climate conditions, may influence the distribution of metals in the soil and water. Hence, the current study aims to discuss the metal origins by investigating metals, EC, salinity, pH and other constituents of the topsoil and water, and statistically analyzing.

2. Materials and methods

2.1. Site description

The study area is located in the north of Baiyin, Gansu province, China (104°10′49″-104°11′06″ E, 36°34′07″-36°34′23″ N). It is within the loess plateau. The chromate plant is on a hillside with the north higher and the south lower, and an artificial channel extends east-west in front of the plant (Figure 1).
Figure 1. The study area and soil, surface and ground water sampling sites.

This area is under arid and semi-arid continental climates, with extremely low precipitation (197 mm/y) and intensive evaporation (1948 mm/y). The soil is weathered from the Late Triassic sandy mudstone. The only aquifer extends as a ribbon along the low-lying area in east-west direction in south of the plant, which is composed of fine to coarse sand and gravel sediments with 4.10-5.60 m thick. The depth of the groundwater table was 0.76-1.50m. The aquifer is recharged by precipitation and the surface water, and discharged mainly through evaporation.

2.2. Soil and water sampling and analysis

The topsoil, surface water and groundwater sampling points are illustrated in Figure 1. 150m×150m grids were laid in the site, and 9 topsoil samples were obtained. Each sample was collected randomly from a grid in the depth of 0-20cm. All soil samples were bagged and sent to the laboratory. In addition, one topsoil sample was collected as a background level on a hill about 800m far away from the site in northwest direction, which is the same soil type as those in the study area. Five monitoring wells were drilled and constructed in the low-lying area, and 5 groundwater samples were collected. Two surface water samples were obtained in the artificial channel, and one was collected upstream to distinguish the influence of this site. Each water sample was collected by an acid washed 1000 ml polyethylene bottle, which was washed 3 times before sampling, and was completely filled with water in case of air bubble trapped. The water samples were carefully sent to the laboratory within 8 hours, and stored at a temperature below 4°C prior to analysis.

The soil samples were air-dried, crushed and passed through a 2 mm sieve. The screened soil particles were used for the subsequent analysis. The soil pH was measured in a 1:2.5 soil/water suspension using a pH meter. Electrical conductivity (EC) was determined in a 1:5 soil/water suspension using a conductivity meter. Soil salinity was analyzed using gravimetric method. To measure metal contents in the soil sample, 0.2g soil solid was digested by a mixture of concentrated hydrochloric acid and nitric acid (3:1 v/v) using a microwave digestion system (YL6C, Changsha Yonglekang Instrument, Ltd., China). As, Cr, Cd, Hg, Fe, Mn, Cu, Pb, Zn, Co, Ni, Sb, Se and V in soil and water were
determined by inductively coupled plasma-optima emission spectrometry (ICP-OES, Optima 5300DV, Perkin-Elmer Instruments, USA), and this work was finished by Shanxi Institute of Engineering Prospecting.

2.3. Extracting tests of chromite and lignite
Extracting tests of the chromite ores and lignite were conducted. Before extracting, 500 g chromite and lignite were respectively ground and screened with 0.15 mm sieve. Mixture of 100 g screened particles and 500 ml distilled water were stirred and then stood in a 1000 ml plastic bottle for 24 h. The suspension was filtered through a 0.45 μm membrane filter, and metal content was measured by the same method described above.

2.4. Statistics
Pearson correlation analysis with 2 tailed was employed to correlate two variables of EC, salinity, pH and metals. Principal component analysis (PCA) was used to extract factors to explain the variances of original variables. The statistics were performed with software SPSS 20.0 for windows.

3. Results and discussion

3.1. EC, salinity, pH and metal concentration of topsoil
The EC, salinity and pH of the topsoil were investigated (table 1), and they are 517.80 to 2600.50 μS/cm, 440.60 to 2060.30 mg/kg and 8.33 to 9.61, respectively, showing a weak to moderate salinization[21]. In comparison with the background level, the soil EC, salinity and pH all increased, which demonstrate that the plant have influenced the soil. Pearson correlation analysis shows the correlation among the three parameters are strong positive with correlation coefficients 0.805 (Salinity/pH), 0.812 (EC/pH) and 0.912 (EC/Salinity). It indicates that the intensive evaporation and leaching of the chromite ores, chromium slags, coal and ash deposits both cause increase of the soil EC, salinity and pH.

It can be observed that Cr, As, Hg, Fe, Se, Ni, Sb and V are the primary contaminants in the topsoil comparing to the background levels. Sum of their CSC is more than 95% and their CSC followed the order: Cr >> V >> Fe >> As > Hg > Ni > Sb > Se. Except for Cr, the other metals all are lower than the Grade II guideline levels (GB15618-2008). According to the extracting tests of the Chromite ores and lignite, Cr, Fe, Hg, Sb, Ni, Co and V in the chromite ores, and Cr, As, Hg, Se and V in the coal, are relatively easily extracted out. Therefore, leaching of the chromite and lignite by rainfall can make these metals increase in the soil. Moreover, ash deposits derived from the combustion are another metal source of the topsoil, especially Hg and As. Concentration of Cu, Zn and Co in the topsoil are lower than their background values, and they may be primarily from geologic origin.

Table 1. EC, salinity, pH and metal concentration in the topsoil and the metals’ CSCa (n=9).

| Component | Value range       | Mean±SD       | CSC(%)       | Background level |
|-----------|-------------------|---------------|--------------|-----------------|
| pH        | 8.33-9.61         | 8.88±0.42     | /            | 8.68            |
| EC (μS/cm)| 517.80-2600.50    | 1190.33±772.12| /            | 428.50          |
| Salinity (mg/kg) | 440.60-2060.30 | 926.67±626.03 | /            | 320.40          |
| Cr (mg/kg) | 33.30-942.10      | 563.66±337.08 | 51.55±18.87  | 3.10            |
| As (mg/kg) | 0.010-0.035       | 0.024±0.011   | 3.17±3.78    | 0.0050          |
| Pb (mg/kg) | N.D.              | /             | /            | /               |
| Cd (mg/kg) | N.D.              | /             | /            | /               |
| Hg (mg/kg) | 0.0001-0.0007     | 0.00036±0.00023| 1.31±0.63   | 0.00010         |
| Fe (mg/kg) | 0.08-7.97         | 3.75±3.35     | 11.32±7.20   | 0.08            |
| Mn (mg/kg) | N.D.              | /             | /            | /               |
| Cu (mg/kg) | 0.20-0.43         | 0.34±0.091    | 0.39±0.23    | 0.37            |
Table 2 shows correlations of each metal with EC, salinity and pH of the soil. Cr, Hg, Fe, Ni and V are moderate to strong positive, while As and Sb strong negative correlation with the soil EC, salinity and pH. It suggests that salinization of the topsoil is probably in favor of accumulation of most metals on the topsoil. Under the alkaline and oxidation condition in the topsoil due to the arid climate, the negatively charged soil is unfavorable for the adsorption of Cr, As, Sb and V, which are dominated in the form of oxyanions[11-12]. Ca\textsuperscript{2+}, Mg\textsuperscript{2+}, K\textsuperscript{+} and Na\textsuperscript{+} can serve as bridges between soil surface and these oxyanions, and show reversible and nonspecific adsorption[13]. PO\textsubscript{4}\textsuperscript{3-}, HCO\textsubscript{3}-, SO\textsubscript{4}\textsuperscript{2-}, Cl\textsuperscript{-} and NO\textsubscript{3}\textsuperscript{-} compete adsorption sites on the soil surface with these oxyanions and promote their mobilization[22-23]. As and Sb can be strongly competed by P anions in the soil adsorption process[14,24]. This may be the main reason that As and Sb both show negative correlation with the salinity and pH. Hg, Ni and Fe usually exist in Hg\textsuperscript{2+}, Hg\textsuperscript{2+}, Ni\textsuperscript{2+} and Fe\textsuperscript{3+} under this Eh-pH condition[15], and cations can compete adsorption sites with them, while anions combine them as HgCl\textsubscript{2}, HgSO\textsubscript{4}, Ni(OH)\textsubscript{2} and Fe(OH)\textsubscript{3}[25], and control their mobility. Therefore, the soil salinization does not certainly enhance accumulation of these metals in the topsoil. It depends on the infiltration of precipitation and the relative contents of Ca\textsuperscript{2+}, Mg\textsuperscript{2+}, Na\textsuperscript{+}, PO\textsubscript{4}\textsuperscript{3-}, HCO\textsubscript{3}-, SO\textsubscript{4}\textsuperscript{2-} and NO\textsubscript{3}\textsuperscript{-}, which are the main constituents of the materials and fuel of the plant. The extremely small precipitation is probably the main reason that the metals concentrate in the topsoil, and leaching of the chromium slags, chromite ores, coal, limestone and dolomite make the topsoil higher contents of these metals, and synchronously higher salinity than the background.

The weak or poor correlations of Cu, Zn, Se and Co with EC, salinity and pH can further demonstrate that there are no significant influences of the salinity in the topsoil in this alkaline range. On the contrary, the metal contamination in the topsoil is primarily from the production process of the chromite. It may be deduced that Cr, As, Hg, Fe, Ni, Sb and V in the topsoil mainly derive from the anthropogenic activities, while Cu, Zn, Se and Co may be primarily from geologic source.

Table 2. Pearson correlation analysis of metal concentration with EC, salinity and pH of the soil (n=9).

|       | EC     | Salinity | pH      |
|-------|--------|----------|---------|
| Cr    | 0.872  | 0.880*   | 0.485   |
| As    | -0.830*| -0.849*  | -0.715  |
| Hg    | 0.859  | 0.883*   | 0.733   |
| Fe    | 0.868**| 0.865**  | 0.763   |
| Cu    | 0.336  | 0.320    | 0.059   |
| Zn    | 0.319  | 0.372    | 0.079   |
| Se    | -0.101 | -0.155   | -0.262  |
| Co    | 0.276  | 0.281    | -0.294  |
| Ni    | 0.870* | 0.864*   | 0.706   |
| Sb    | -0.730 | -0.707   | -0.802* |
| V     | 0.743* | 0.708**  | 0.516   |

* Correlation is significant at 0.05 level (2 tailed).
** Correlation is significant at 0.01 level (2 tailed).
3.3. Correlation between metals

Significantly strong correlations are found among some metals (table 3). Cr, Fe, Ni, V and Hg are the main constituents of the chromite ores or the coal. Their positive correlations indicate that there are influences of leaching of the pollution resources of the plants on their concentration in the topsoil. The negative correlation between As and Fe may reveal that the alkaline condition of the soil is unfavorable for the adsorption of As on the iron bearing minerals[26].

Cr/Cu, Cr/Zn, Cr/Co, Hg/Fe, Hg/Zn, Hg/Ni, Fe/Cu, Cu/Co, Cu/Ni, Cu/V and Se/V show moderate positive correlations, while chalcophilic elements such as Cu, Zn, Sb and Hg show weak or poor correlations. It indicates that leaching of the chromite ores, chromium slags, coal and the ash deposits are still the main source of the soil metals, although Cu and Zn are not the main associate elements of the chromite and coal.

The negative moderate correlations of As/Zn, As/Ni, Se/Hg, Se/Zn, Sb/Hg, Sb/Fe and Sb/Ni may imply that these metals host different adsorption behavior in the soil due to the predominant species of HAsO$_4^{2-}$, SeO$_2^-$ and Sb(OH)$_6^{2-}$ and Zn$^{2+}$, Ni$^{2+}$, Hg$^{2+}$ and Fe$^{3+}$ under this alkaline and oxidation environments[11].

Table 3. Pearson correlation analysis among metal concentrations in the soil (n=9).

|       | Cr   | As    | Hg    | Fe   | Cu    | Zn    | Se    | Co    | Ni    | Sb    | V     |
|-------|------|-------|-------|------|-------|-------|-------|-------|-------|-------|-------|
| Cr    | 1    |       |       |      |       |       |       |       |       |       |       |
| As    | -0.678 | 1     |       |      |       |       |       |       |       |       |       |
| Hg    | 0.809* | -0.613 | 1     |      |       |       |       |       |       |       |       |
| Fe    | 0.895* | -0.893 | *     | 0.770 | 1     |       |       |       |       |       |       |
| Cu    | 0.715  | -0.296 | 0.301 | 0.582 | 1     |       |       |       |       |       |       |
| Zn    | 0.608  | -0.621 | 0.611 | 0.380 | 0.261 | 1     |       |       |       |       |       |
| Se    | -0.069 | 0.412  | -0.549 | -0.20 | 0.483 | -0.594 | 1     |       |       |       |       |
| Co    | 0.577  | -0.188 | 0.057  | 0.259 | 0.739 | 0.521 | 0.369 | 1     |       |       |       |
| Ni    | 0.834* | -0.730 | 0.757  | 0.880* | 0.552 | 0.226 | -0.155 | 0.071 | 1     |       |       |
| Sb    | -0.328 | 0.666  | -0.580 | -0.655 | 0.016 | 0.156 | 0.071 | 0.371 | -0.664 | 1     |       |
| V     | 0.778* | -0.448 | 0.392  | 0.776* | 0.752 | -0.142 | 0.544 | 0.334 | 0.749* | 0.493 | 1     |

To further understand the impact factors on the soil metals, PCA was employed to reduce the number of the variables (table 4). Three factors were separated and they explain 96.64% of the variance using 11 variables. Factor I explains 54.58% of the total variance, and has a loading from the concentration of Cr, Fe, Ni (>90%), As, Hg (>80%), and V (>70%). A very high loading of Cr, Fe and Ni indicates a strong correlation of the soil pollution with the chromite ores, while high loading of As, Hg and V with the lignite and partly the chromite. Factor II and factor III explain 23.38% and 18.66% of the total variance, and respectively has a loading of Se (>90%), Cu (>70%), Co (>60%) and Zn (>80%), Sb (>70%). It reveals that these metals in the soil are mainly from geologic origin, which can be confirmed by their concentrations approximating to the background levels.

Table 4. Results of the factor analysis showing relative loading from the 11 metals in the soil.

|       | Factor I | Factor II | Factor III |
|-------|----------|-----------|------------|
| Cr    | 0.956    | 0.146     | 0.234      |
| As    | -0.887   | 0.359     | -0.048     |
| Hg    | 0.887    | -0.441    | 0.056      |
| Fe    | 0.985    | -0.026    | -0.158     |
| Cu    | 0.654    | 0.706     | 0.215      |
| Zn    | 0.499    | -0.310    | 0.802      |
| Se    | -0.118   | 0.926     | -0.328     |
3.4. Origin of metals in the surface water
Comparing to the reference value (table 5), As, Cr, Fe, Hg and Ni in the artificial channel increase apparently after water run through the site, especially Cr and Fe, which increase from N.D. (not detected) to 33.59 and 39.90 mg/l, respectively. It indicates that this site posed significant influences on the surface water. Increase of pH, TDS and salt ions, particularly increase of Na\(^+\), Ca\(^{2+}\), Mg\(^{2+}\), HCO\(_3\)\(^-\) and SO\(_4\)\(^{2-}\) are attributed to the calcite roasting technique, which can further demonstrate that the metals in the surface water are mainly from the plant.

### Table 5. Descriptive statistics of chemical parameters of the groundwater and the surface water.

| Parameter | Surface water (mg/l) | Groundwater (mg/l) (n=5) |
|-----------|----------------------|--------------------------|
|           | Monitoring data | Reference value | Min | Max | Mean±SD |
| pH        | 7.99        | 7.67 | 7.55 | 7.87 | 7.80±0.14 |
| K\(^+\)    | 174.28      | 32.41 | 19.65 | 36.14 | 28.53±7.75 |
| Na\(^+\)   | 697.33      | 719.02 | 390.17 | 551.06 | 494.72±62.22 |
| Ca\(^{2+}\) | 626.33      | 305.63 | 103.20 | 460.90 | 331.66±141.09 |
| Mg\(^{2+}\) | 167.12      | 94.20 | 21.30 | 182.30 | 81.06±64.09 |
| HCO\(_3\)\(^-\) | 463.70      | 268.50 | 189.20 | 509.50 | 305.28±129.91 |
| Cl\(^-\)    | 1666.20     | 1045.80 | 170.20 | 1329.40 | 588.18±437.84 |
| SO\(_4\)\(^{2-}\) | 5703.70     | 1056.70 | 355.40 | 1329.40 | 1560.02±1261.76 |
| NO\(_3\)\(^-\) | 181.36      | 103.46 | 2.48 | 99.11 | 26.52±40.82 |
| TDS        | 11546.85    | 3700.20 | 712.20 | 7712.40 | 3482.80±2812.14 |
| Cr         | 39.90       | N.D. | 0.005 | 0.332 | 0.118±0.139 |
| As         | 0.003       | 0.002 | 0.001 | 0.018 | 0.0098±0.0083 |
| Fe         | 33.59       | N.D. | 0.090 | 0.252 | 0.114±0.076 |
| Mn         | N.D.        | N.D. | 0.050 | 2.64 | 0.76±1.11 |
| Cu         | 0.080       | 0.049 | N.D. | N.D. | N.D. |
| Pb         | N.D.        | 0.002 | 0.0011 | 0.083 | 0.037±0.039 |
| Cd         | N.D.        | N.D. | 0.0010 | 0.0323 | 0.0124±0.0134 |
| Ni         | 0.0059      | 0.0023 | 0.008 | 0.012 | 0.0092±0.0027 |
| Hg         | 0.00009     | 0.00006 | 0.00005 | 0.00012 | 0.000062±0.000022 |

3.5. Origin of metals in the groundwater
Groundwater is weak alkaline and low-moderate mineralization, and is characterized by high Na\(^+\), Ca\(^{2+}\), Cl\(^-\), SO\(_4\)\(^{2-}\) and HCO\(_3\)\(^-\) (table 5), which reveals that the plant has influenced the groundwater. Cr, As, Fe, Mn, Pb, Cd, Ni and Hg were detected in the groundwater, where Cr, Mn, Pb, Cd in part of the monitoring wells are higher than their Grade III guideline levels (GB/T 14848-2017). From the results of the soil metal contamination (table 1), Mn, Pb and Cd were not detected in the topsoil, which suggests that these elements in the groundwater are probably from the geologic origin. Based on PCA for the groundwater samples (Figure 2), Principal Component 1 (PC1) and Principal Component 2 (PC2) respectively explain 41.57% and 35.88% of variance in the dataset. PC1 has a high loading for Cr, Fe, Ni, Hg and NO\(_3\)\(^-\). It represents the impacts of the chromite and lignite, which is in accordance with the results of the topsoil. PC2 has a high loading for Ca\(^{2+}\), Mg\(^{2+}\), Cl\(^-\), SO\(_4\)\(^{2-}\) and HCO\(_3\)\(^-\), revealing the influence of the arid climate, surface water discharge, and utilization of limestone, dolomite, and
lignite. The low to intermediate loading for Cd (positive), Mn and Pb (negative) may imply their geologic origin. Intermediate loading of Na\textsuperscript{+} in PC1 and PC2 represents the impacts of using of soda and the evaporation.

Figure 2. Loading of the components in the groundwater.

4. Conclusion
The strong positive correlations among EC, salinity and pH are attributed to the extensive evaporation and leaching of the chromite ores, lignite, limestone and dolomite. The extremely small precipitation is responsible for the accumulation of metals in the topsoil, and influences of the soil salinization on the metal fate and transport depend on the relative contents of Ca\textsuperscript{2+}, Mg\textsuperscript{2+}, Na\textsuperscript{+}, PO\textsubscript{4}\textsuperscript{3-}, HCO\textsubscript{3}\textsuperscript{-} and SO\textsubscript{4}\textsuperscript{2-}. Cr, Fe, Ni, As, Hg, V and Sb in the topsoil correlate with the chromite ores and lignite, and Se, Cu, Co, and Zn are mainly from geologic origin. Increase of As, Cr, Fe, Hg and Ni in the artificial channel reveals the influence of the plant. Groundwater in the area is weak alkaline and low-moderate mineralization, and the high contents of Ca\textsuperscript{2+}, Mg\textsuperscript{2+}, Cl\textsuperscript{-}, SO\textsubscript{4}\textsuperscript{2-} and HCO\textsubscript{3}\textsuperscript{-} reveal the influence of the arid climate, surface water and utilization of limestone, dolomite and lignite. The high Na\textsuperscript{+} in the groundwater represents the impacts of using of sodium carbonate. Cr, Fe, Ni and Hg in the groundwater primarily derive from chromite ores and lignite, and Cd, Mn and Pb may be related to their geologic origin. Therefore, it can be concluded that the factory synchronously makes the soil metals, EC, salinity and pH increase, and the salinization conversely influence the fate and transport of the metals. Leaching of the polluted soil further pollutes the groundwater and surface water.

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References
[1] Amphalop, N., Suwantarat, N., Prueksasit, T., Yachusri, C., Srithongouthai, S. (2020) Ecological risk assessment of arsenic, cadmium, copper, and lead contamination in soil in e-waste separating household area, Buriram province, Thailand. Environmental Science and Pollution Research. https://doi.org/10.1007/s11356-020-10325-x.
[2] Ennaji, W., Barakat, A., El Baghdadi, M., Rais, J. (2020) Heavy metal contamination in agricultural soil and ecological risk assessment in the northeast area of Tadla plain, Morocco. Journal of Sedimentary Environments, 5:307-320.

[3] Liu, J. S., He, H. C. (2018) Identifying the Origins and Spatial Distributions of Heavy Metals in the Soils of the Jiangsu Coast. Environmental Science, 39(6):2853-2864.

[4] Bilguun, U., Namkhaiyambuu, D., Purevsuren, B., Soyol-Erdene, T-O., Tuuguu, E., Daichaa, D.(2020) Sources, Enrichment, and Geochemical Fractions of Soil Trace Metals in Ulaanbaatar, Mongolia. Archives of Environmental Contamination and Toxicology, 79:219-232.

[5] Zhao, S., Feng, C.H., Wang, D.X., Liu, Y.Z., Shen, Z.Y.(2013) Salinity increases the mobility of Cd, Cu, Mn, and Pb in the sediments of Yangtze Estuary: Relative role of sediments’ properties and metal speciation. Chemosphere, 91(7): 977-984.

[6] Pontoni, L., van Hullebusch, E.D., Pechaud, Y., Fabbricino, M., Esposito, G., Pirozzi, F.(2016) Colloidal Mobilization and Fate of Trace Heavy Metals in Semi-Saturated Artificial Soil (OECD) Irrigated with Treated Wastewater. Sustainability, 8(12):1257-1266.

[7] Fernández, M.A., Soulages, O.E., Acebal, S.G., Rueda, E.H., Sánchez, R.M. T. (2015) Sorption of Zn(II) and Cu(II) by four Argentinean soils as affected by pH, oxides, organic matter and clay content. Environmental Earth Sciences, 74(5):4201-4214.

[8] Lange, B., Pourret, O., Meerts, P., Jitaru, P., Cances, B., Grison, C., Faucon, M.-P. (2016) Copper and cobalt mobility in soil and accumulation in a metallophyte as influenced by experimental manipulation of soil chemical factors. Chemosphere, 146: 75-84.

[9] Kuang, G. X., Wu, Y. Q., Li, C. L. (2010) The soil characteristics and planting division in Lanzhou-Baiyun area. Gansu Science and Technology, 26(17): 168-171.

[10] Xi, J.H., He, M.C., Wang, K.P., Zhang, G.Z. (2013) Adsorption of antimony (III) on goethite in the presence of competitive anions. Journal of Geochemical Exploration, 132: 201-208.

[11] Nakamaru, Y. M., Altansuvd, J. (2014) Speciation and bioavailability of selenium and antimony in non-flooded and wetland soils: A review. Chemosphere, 111: 366-371.

[12] Rajput, S., Pittman, Jr C.U., Mohan, D.(2016) Magnetic magnetite (Fe₃O₄) nanoparticle synthesis and applications for lead (Pb²⁺) and chromium (Cr⁶⁺) removal from water. Journal of Colloid and Interface Science, 468: 334-346.

[13] Bhattacharyya, K.G., Gupta, S.S. (2008) Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: a review. Adv. Colloid Interf. Sci., 140: 114-131.

[14] Chen, H.W., Liu, L., Gong, R.Y., Wei, R.C., Yi, Q.H., Qiu, A.N. (2016) Comparison of Kinetics of Arsenic(V) Adsorption on Two Types of Red Soil Weathered from Granite and Sandstone. Water, Air, & Soil Pollution, 227: 406-416.

[15] Reis, A.T., Coelho, J. P., Rucandio, I., Davidson, C. M., Duarte, A.C., Pereira, E. (2015) Thermo-desorption: A valid tool for mercury speciation in soils and sediments? Geoderma, 237-238: 98-104.

[16] Smedley, P. L., Kinniburgh, D.G. (2002) A review of the source, behavior and distribution of arsenic in natural waters. Applied Geochemistry, 17: 517-568.

[17] Zheng, S.A., Zheng, X.Q., Chen, C. (2013) Transformation of metal speciation in purple soil as affected by waterlogging. International Journal of Environmental Science and Technology, 10(2): 351-358.

[18] Owojori, O. J., Siciliano, S. D.(2015) The potentiation of zinc toxicity by soil moisture in a boreal forest ecosystem. Environ Toxicol Chem., 34(3): 600-607.

[19] Rubie, D.C., Laurenz, V., Jacobson, S.A., Morbidelli, A., Palme, H., Vogel, A.K., Frost, D. J.(2016) Highly siderophile elements were stripped from Earth’s mantle by iron sulphide segregation. Science, 353(6304):1141-1144.

[20] Harvey, J., Day, J.M.D. (2016) Introduction to highly siderophile and strongly chalophile elements in high temperature geochemistry and cosmochemistry. Mineralogical Society of America, 81(1): 3-14.
[21] Wang, J.Z., Wu, J.L., Jia, H.J. (2016) Analysis of Spatial Variation of Soil Salinization Using a Hydrochemical and Stable Isotopic Method in a Semi-arid Irrigated Basin, Hetao Plain, Inner Mongolia, North China. Environmental Processes, 3(4): 723-733.

[22] Badruddoza, A.Z.Md., Shawon, Z.B.Z., Rahman Md. T., Hao, K.W., Hidajat, K., Uddin, M.S. (2013) Ionically modified magnetic nanomaterials for arsenic and chromium removal from water. Chemical Engineering Journal, 225: 607-615.

[23] Arco-Lázaro, E., Agudo, I., Clemente, R., Bernal, M. P. (2016) Arsenic(V) adsorption-desorption in agricultural and mine soils: Effects of organic matter addition and phosphate competition. Environmental Pollution, 216: 71-79.

[24] Rouwane, A., Rabiet, M., Grybos, M., Bernard, G., Guibaud, G. (2016) Effects of NO$_3^-$ and PO$_4^{3-}$ on the release of geogenic arsenic and antimony in agricultural wetland soil: a field and laboratory approach. Environmental Science and Pollution Research, 23(5): 4714-4728.

[25] Wang, J.X., Feng, X.B., Anderson, C.W.N., Xing, Y., Shang, L.H. (2012) Remediation of mercury contaminated sites - A review. Journal of Hazardous Materials, 221-222: 1-18.

[26] Chen, H.W., Mei, J.H., Luo, Y.P., Qi, A.N., Wang, H. (2017) Adsorptive properties of alluvial soil for arsenic(V) and its potential for protection of the shallow groundwater among Changsha, Zhuzhou, and Xiangtan cities, China. Environ Sci Pollut Res., 24:4018-4028.