

Geochemistry and contents of trace metals in the soils and sediments of Daliao River System watershed, China

Mengchang He, Xitao Liu and Chunye Lin

State Key Joint Laboratory of Environmental Simulation and Pollution Control, School of Environment, Beijing Normal University, Beijing 100875, China. Email c.lin@bnu.edu.cn

Abstract

The Daliao River System (DRS) watershed has the long-term been affected by intensive industrial, urban and agricultural activities. The objectives of this study were to compare contents of trace metals and geochemical relationships between trace metals and Mn in the watershed soils and estuarine sediments of the DRS. Thirty five surface sediment samples were collected from the DRS estuary and analysed for trace metals. Trace metal contents in the various soils of the DRS watershed were collected from the earlier survey in the 1980s. Results indicate that As, Cr, Cu, Hg, Ni, Pb and Zn contents and their geochemical baselines in the estuarine sediments were similar to those in the watershed soils. However, Cd content was much higher in the estuarine sediments than in the watershed soils, while Co and V contents in the estuarine sediments were much lower. Higher Cd content in the estuarine sediments might be caused by contamination; while lower Co and V contents might be caused by the sedimentary environment, resulting in release of Co and V in the sediments. Our study documented that the geochemical baselines of most trace metals for the watershed soils were generally similar to those for the estuarine sediments of the DRS.

Key Words

Trace metals, soils, sediments, estuary, watershed.

Introduction

The products of rock weathering constitute most of the inorganic minerals in soils and sediments. In addition, aquatic sediments generally originate from erosion of soils. Therefore, elemental composition and geochemistry in soils are generally similar to those in sediments in the same watershed (Bowen, 1979). However, internal and external factors, such as contamination, precipitation, dissolution, postdepositional effects of diagenesis, etc., might change elemental composition and geochemistry in sediments (Forstner and Wittmann 1983). Thus, a knowledge of elemental geochemical relationship from soils to sediments is of considerable importance in understanding the elemental geochemistry and contamination within watersheds.

The Daliao River System (DRS) consists of the Daliao river, Hun river, and Taizi river, with 94 km, 415 km, and 413 km in length, and draining 1390 km², 11500 km², and 13900 km² of land area, respectively (Figure 1). The DRS is the most important water course in Liaoning Province of China. These rivers drain large industrial, urban and agricultural areas. Average annual outputs of Cu, Pb and Zn were 70.3×10³, 40.3×10³ and 265.9×10³ t, respectively, in the province during the period of 1990 to 2006. In addition, the output of pig iron reached 37.6×10⁶ t in 2006. Big industrial cities in the watershed of the DRS include Fushun, Shenyang, Benxi, Anshan, Liaoyang, Panjin, and Yingkou, with populations of 2.24, 6.98, 1.56, 3.47, 1.82, 1.25, 2.30 million, respectively, in 2005. Hence, there is interest in investigating composition and geochemistry of the trace metals in the soils and sediments of the DRS watershed. The objectives of this study were to compare contents of trace metals and geochemical relationships between trace metals and mineral matrix element Mn in the watershed soils and estuarine sediments of the DRS.

Methods

Data collection

Elemental contents in the soils of DRS watershed as well as Liaoning province were investigated in 1980s, for thousands of soil samples. We collected the data on contents of trace metals (As, Cd, Co, Cr, Cu, Hg, Ni, Pb, V, and Zn) and mineral matrix element Mn in various types of soil obtained by this investigation.

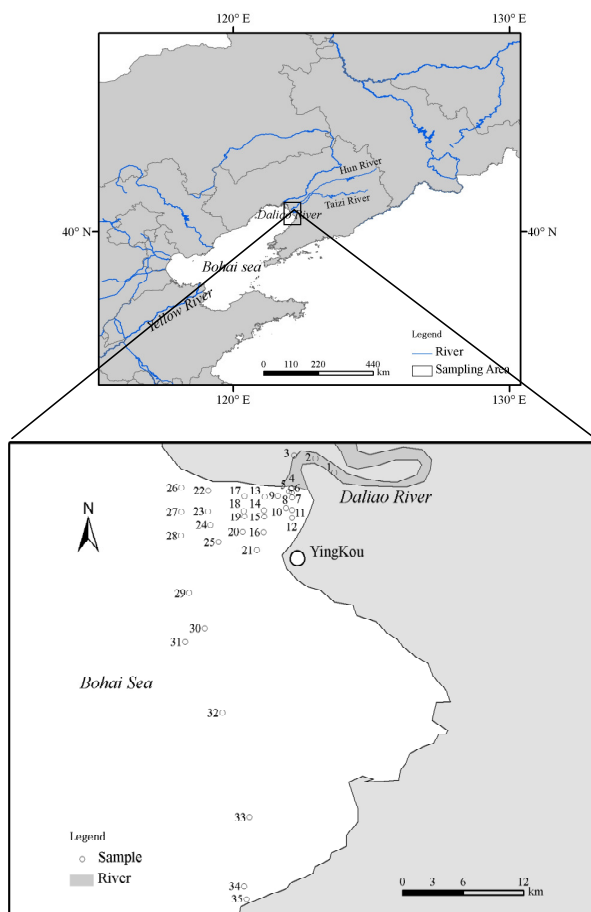


Figure 1. Schematic graph of DRS watershed and sediment sampling sites.

10.02%, 6.01%, 5.10%, 6.74%, 3.81%, 2.27%, 6.21%, 1.65%, 2.75%, 1.99% and 1.52% for As, Cd, Co, Cr, Cu, Hg, Ni, Pb, V, Zn, Mn, Al, Fe and Ca, respectively.

Results

Comparison between elemental contents in the estuarine sediments and watershed soils of the DRS

The contents of Mn, Al, Fe and Ca in the estuarine sediments of the DRS were 264.7-1073.0 mg/kg, 3.77-7.97%, 0.67-4.19% and 0.75-2.02%, respectively, with means of 623.9 mg/kg, 6.72%, 2.61% and 1.20%. Compared with world average contents of 770 mg/kg, 7.2%, 4.1% and 6.6% of Mn, Al, Fe and Ca, respectively (Bowen, 1979), the surface sediments of the estuary contained slight lower Mn, Al and Fe and much lower Ca. The average contents of As, Cd, Co, Cr, Cu, Hg, Ni, Pb, V and Zn in the estuarine sediments of the DRS were 10.68, 0.39, 10.60, 65.20, 21.06, 0.06, 23.47, 26.19, 62.37, 76.62 mg/kg, respectively; while in the watershed soils of the DRS they were 8.90, 0.12, 15.36, 52.21, 22.54, 0.04, 27.03, 22.05, 82.40 and 67.93 mg/kg, respectively (Figure 2).

As, Cr, Cu, Hg, Ni, Pb and Zn contents in the estuarine sediments were similar to those in the watershed soils. This may indicate that these trace metals in the estuarine sediments mainly originated from soil erosion of watershed as natural source. On the other hand, Cd content was much higher in the estuarine sediments than in the watershed soil, while Co and V contents were much lower in the estuarine sediments than in the

Sediment sampling and analysis

Surface sediment samples were collected at 35 sites within the estuarine coastal area in 2007, using cable operated sediment samplers (Van Veen grab sampler, Eijkelkamp) (Figure 1). All sediment samples were freeze-dried, slightly crushed, passed through 2 mm sieve, and stored in glass bottles.

Portions of the sediment samples were digested with HNO₃-HF-HClO₄ and the filtrated extracts were measured for Co, Cr, Cu, Hg, Ni, V, Zn, Mn, Al, Fe and Ca by ICP-OES (IRIS Intrepid II, Thermo Electron) and for Cd and Pb by ICP-MS (X Series II, Thermo Electron) (Lin *et al.* 2008). In addition, sediment samples were digested with aqua regia, 1% KMnO₄ solution, and 1% oxalic acid, with the supernatant was measured by atomic fluorescence spectroscopy (XGY-1011A, Institute of Geophysical and Geochemical Exploration, Chinese Academy of Geological Sciences) for As and Hg concentrations. The accuracy of the method was assessed by conducting analyses of three reference materials (GSS1, GSS2, GSS9) from Institute of Geophysical and Geochemical Exploration, Chinese Academy of Geological Sciences. Average relative errors (triplicate) of As, Cd, Co, Cr, Cu, Hg, Ni, Pb, V, Zn, Mn, Al, Fe and Ca for the three reference materials were -1.7~1.0%, -5.2~12.5%, -1.8~1.9%, -6.0~1.7%, 4.5~7.67%, -1.3~4.2%, -2.0~7.8%, -0.9~5.0%, -3.3~2.8%, -4.7~7.1%, -1.9~-0.1%, -1.6~3.1%, -0.1~2.7% and 1.2~2.0%, respectively. The precision was calculated as the variation coefficients (CV%) of two replicates from 14 sediment samples, and average CV% was 4.51%, 8.92%, 4.03%,

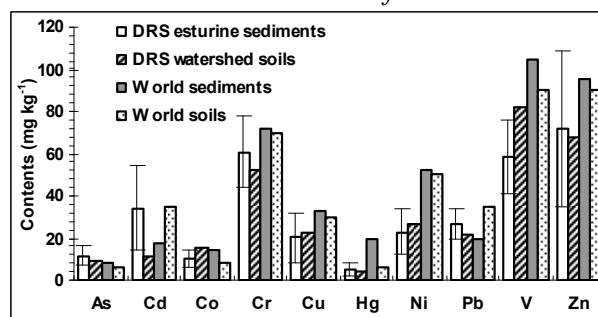
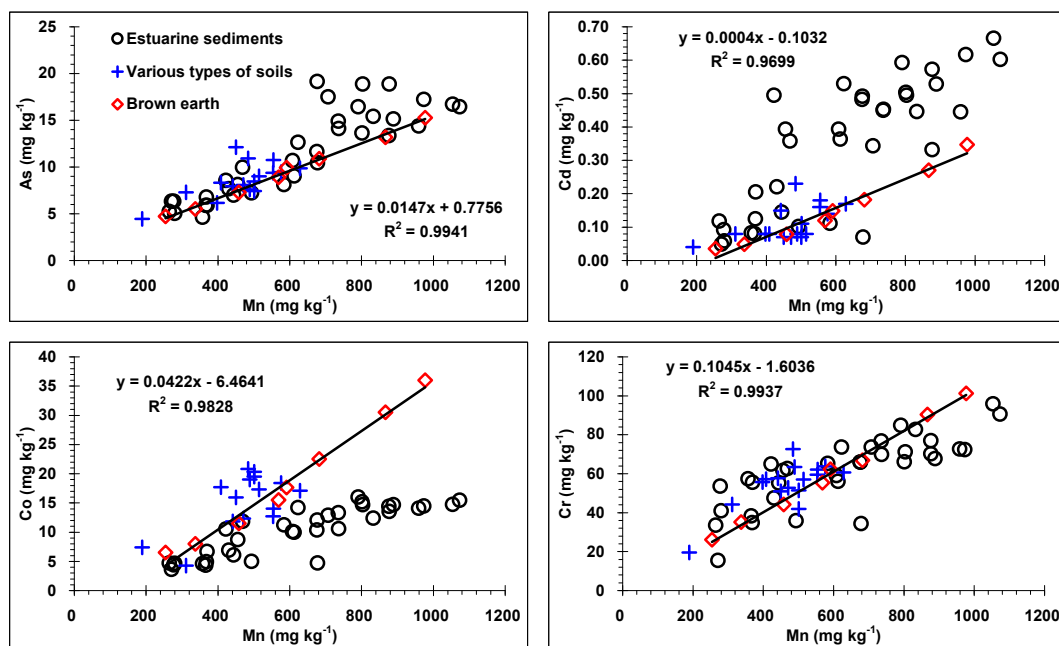


Figure 2. Trace metal contents in the watershed soils and sediments of the DRS and world sediments and soils (Bowen, 1979).

watershed soils. The higher Cd content in the estuarine sediments indicated its anthropogenic sources such as industrial and municipal effluent. The lower Co and V contents in the estuarine sediments may show their dissolution, following sedimentation of suspended particles. In addition, whereas Cd and Pb contents in the watershed soils of the DRS were much lower than those in the world soils, Cd and Pb contents in the estuarine sediments of the DRS were higher than those in the world sediments (Figure 2), indicating relatively higher enrichment of Cd and Pb in the estuarine sediments. This might be related to the Pb mining and smelting in the watershed. Cu, Ni and Zn contents in the both soils and estuarine sediments of the DRS were much lower than those in the world soils and sediments.

Comparison between elemental geochemical relationships in the estuarine sediments and watershed soils of the DRS

Trace metal contents in the soils and estuarine sediments were plotted as function of the content of mineral matrix element Mn (Figure 3). Trace metal contents were positively correlated with Mn content in the both watershed soils and estuarine sediments of the DRS. In non-contaminated soils and sediments, trace element contents are generally correlated significantly with the contents of co-occurring elements or mineral matrix elements and the regression lines (equations) are defined as the geochemical baselines of trace metals for soils and sediments (Windom, 1989). The cross symbol in Figure 3 represents average contents of elements in the various types of the watershed soils, including brown earths, weakly brown earths, aquic brown earths, dark-brown earths, meadow soils, cinnamon soils, leached cinnamon soils, calcic cinnamon soils, meadow soils, calcic meadow soils etc. The square symbol in Figure 3 represents elemental content average and percentiles at 5%, 10%, 25%, 50%, 75%, 90%, and 95% of 267 soil samples of brown earths covering the most area of the watershed. For As, Cr, Cu, Hg, Ni, Pb and Zn, their geochemical relationships with Mn in the watershed soils were similar to those in the estuarine sediments. However, Cd content was relatively higher and Co and V contents were relatively lower in the estuarine sediments. Generally, changes of geochemical conditions from soils to sediments and contamination can change geochemical relationships of trace metals with co-occurring elements or mineral matrix elements. Relatively higher Cd content in the estuarine sediments might be caused by contamination; while relatively lower Co and V contents might be caused by the geochemical conditions of the estuarine sediments, resulting in release of Co and V in the sediments. The regression lines (equations) were fitted with datum points of square symbol (Figure 3), indicating trace metals contents were significantly correlated to the mineral matrix Mn in the brown earths covering the most area of the watershed. For As, Cr, Cu, Ni, Pb, and Zn, the regression lines generally fitted well datum points for the estuarine sediments, indicating similar geochemical relationships between trace elements and Mn in the watershed soils and estuarine sediments. Therefore, these regression lines might be geochemical baselines of the trace metals in the watershed soils and estuarine sediments to identify their sources and contamination.



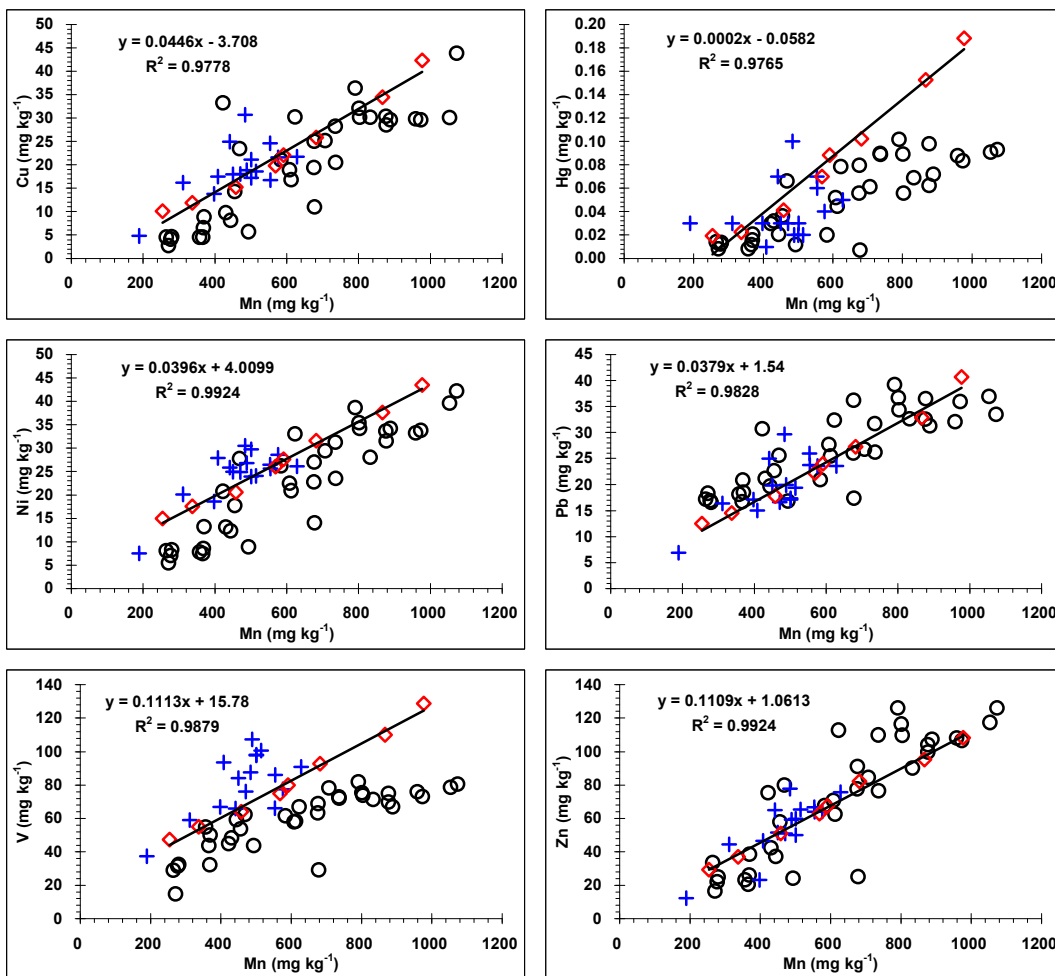


Figure 3. Geochemical relationship between trace metal contents and mineral matrix element Mn content in the watershed soils and estuarine sediments of the DRS. The detailed explanation are given in text.

Conclusion

As, Cr, Cu, Hg, Ni, Pb and Zn contents in the estuarine sediments were similar to those in the watershed soils, indicating that these trace metals mainly originated from soil erosion of watershed as natural source. On the other hand, anthropogenic input of Cd into the DRS led to the higher content of Cd in the estuarine sediments, but dissolution of V and Co, caused by the estuarine sedimentary condition, resulted in the lower content of V and Co in the estuarine sediments. The geochemical relationships of As, Cr, Cu, Hg, Ni, Pb and Zn with Mn in the watershed soils were similar to those in the estuarine sediments, documenting the geochemical baselines of these trace metals were similar in the watershed soils and estuarine sediments of the DRS.

Acknowledgements

This study was supported by the National Basic Key Research Program of China (2004CB418502) and the National Natural Science Foundation of China (40971058, 40873077).

References

- Bowen HJM (1979) 'Environmental Chemistry of the Elements.' (Academic Press: London)
- Försterner U, Wittmann GTW (1981) 'Metal Pollution in the Aquatic Environment, 2nd edn.' (Springer Verlag: Berlin)
- Lin C, He MC, Zhou YX, Guo W, Yang ZF (2008) Distribution and contamination assessment of heavy metals in sediment of the Second Songhua River, China. *Environ. Monit. Assess.* **137**, 329-342.
- Windom HL, Schropp SJ, Calder FD, Ryan JD, Smith RG, Burney LC, Lewis FG, Rawlinsont CH (1989) Natural trace metal concentrations in estuarine and coastal marine sediments of the Southeastern United States. *Environ. Sci. Technol.* **23**, 314-320.